



Theory of sampling - a mini seminar under the NKS project SAMPSTRAT

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Theory of Sampling – a mini seminar under the NKS project SAMPSTRAT

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April 2006

Abstract

At an emergency situation a large number of matrixes can be contaminated and samples of these different matrixes will be collected. These sample matrixes might be or often certainly are heterogeneous and in general more unevenly distributed than from nuclear test fallout or even the Chernobyl accident. On basis of the reported data conclusions and remedial actions causing social and economical costs for the society are taken. Therefore the number of samples from each site, their size and further homogenisations is of great importance. In the case of an emergency situation the activities are generally high and the errors due to counting statistics are small. We could also imagine a situation when a certain nuclear enterprise/activity has to close down or being prosecuted, based on sampling and analysis, for not following directives of discarding radioactivity in the environment. We therefore organized a seminar focusing on the above mentioned problems.

The seminar covered several important topics such as an introduction to Theory of sampling (TOS), Lot heterogeneity and sampling in practice, Statistics for sampling in analytical chemistry, Representative mass reduction in sampling. Case studies were presented such as Sampling of heterogeneous bottom ash from municipal waste-incineration plants and Sampling and inventories at Thule Greenland, which also illustrated the difficulties with Plutonium Inventory Calculations in Sediments when Hot Particles were present.

Key words

Sampling, Sampling characteristics, Small sub sampling, Heterogeneous, Particles, Theory of Sampling, TOS, Municipal waste, Bottom ash, Data analysis reliability, variances, Statistics of counting, The minimum practical error, Measuring limitations

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Theory of Sampling – a mini seminar under the NKS project SAMPSTRAT

26 August 2005, Risø, Denmark

Edited by E. Holm

Organizers. Elis Holm, Lars Frøsig Østergaard Rajdeep Sidhu

Foreword

At an emergency situation a large number of matrixes can be contaminated and samples of these different matrixes will be collected. These sample matrixes might be or often certainly are heterogeneous and in general more unevenly distributed than from nuclear test fallout or even the Chernobyl accident. On basis of the reported data conclusions and remedial actions causing social and economical costs for the society are taken. Therefore the number of samples from each site, their size and further homogenisations is of great importance. In the case of an emergency situation the activities are generally high and the errors due to counting statistics are small. We could also imagine a situation when a certain nuclear enterprise/activity has to close down or being prosecuted, based on sampling and analysis, for not following directives of discarding radioactivity in the environment.

It is not uncommon that it is the same person who makes the sampling, the sample preparation, the radiochemical separation, the subsequent measurements and the data analysis/conclusions. It is our feeling that especially the sampling part is given less attention compared to the other steps.

The Theory Of Sampling is a description of all errors involved in sampling of heterogeneous material. Data analysis are often regarded as separate from analysis and especially separated from the process producing the sample, upon which depend both radiochemical analysis and/or measurement. Data are not separate entities, which can be dealt with alone-in fact data do not exist until after analysis has taken place. Someone has to assume the responsibility for obtaining representative samples prior to analysis. Without being representative in this first stage in the entire analytical chain, there is no way of ever evaluating the degree of sampling bias and sampling errors associated with the final result. Within radioecology the Theory of sampling has often not been applied as it should be or even neglected.

From experience it is known that the sampling errors typically amount to 10-100, or even as much as 100-1000 times the specific analytical errors. The project has the aim to develop a Theory Of Sampling for the assessment of radioactivity under emergency situations. For this purpose Fundamental Sampling Principles must be given special attention. The sharing of efforts between sampling, radiochemical separation and/or measurement and data analysis must be better balanced.

The theory of sampling has been better developed within other environmental sciences than radioecology. We hope to learn something from what is known in these fields and apply this on assessment of radioactive contamination.

We therefore organized a seminar focusing on the above mentioned problems the first year. On basis of the outcome from the seminar a proposal for practical work can be given. At the end the ultimate aim is to give recommended methods for sampling and sample preparations in emergency situations. This would also be useful for routine research in environmental radioactivity studies. For all students in Environmental Radioactivity, and other people performing sampling in general and under emergency situations a course in Theory of Sampling would be appropriate.

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Theory of Sampling
NKS Seminar, August 26, 2005.
Risø, Denmark

Agenda:

10:00 - 10:30 Gathering and coffee

10.30 – 12:00 **Kim Esbensen**. Theory of sampling (TOS)-an introduction: Lot heterogeneity and sampling in practice.

12:00 – 12.45 **Lars Petersen**. Representative mass reduction in sampling.

12.45 –13.45 Lunch

13:45 – 14:30 **Hans Møller**. Sampling of heterogenous bottom ash from municipal waste-incineration plants.

14:30 – 15:15 **Bo Svensmark**. Statistics for sampling in analytical chemistry.

15:15 - 16:00 **Mats Eriksson**. Sampling and inventories at Thule Greenland. A case study.

16:00 -16:30 Coffee

16:30 – 17:00. General discussion

Elis Holm Lars Frøsig Østergaard Rajdeep Sidhu

Lecturers and participants

Lecturers:

Hans Møller (Elsam A/S)
Bo Svensmark (Københavns Universitet)
Kim Esbensen (Syddansk Universitet)
Mats Eriksson (Marine Environmental Laboratory, IAEA)

Participants:

Cathrin Lind
Sara Almgren
Anne Liv Rudjord
Torbjörn Gäfvert
Gertie Johansson
Birgit Amilon
Bredo Möller
Elisabeth Strålberg
Rajdeep Sidhu
Inger Eikermann
Kenn Skönninge
Jon Bering
Sigurdur Emil Palsson
Per Roos
Xiaolin Hou
Sven Nielsen
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Representative sampling for reliable data analysis: Theory of Sampling

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Abstract

The Theory of Sampling (TOS) provides a description of all errors involved in sampling of heterogeneous materials as well as all necessary tools for their evaluation, elimination and/or minimization. This tutorial elaborates on—and illustrates—selected central aspects of TOS. The theoretical aspects are illustrated with many practical examples of TOS at work in typical scenarios, presented to yield a general overview. TOS provides a full scientific definition of the concept of *sampling correctness*, an attribute of the sampling process that must never be compromised. For this purpose the Fundamental Sampling Principle (FSP) also receives special attention. TOS provides the first complete scientific definition of *sampling representativeness*. Only correct (unbiased) mass reduction will ensure representative sampling. It is essential to induct scientific and technological professions in the TOS regime in order to secure the necessary reliability of: *samples* (which must be representative, from the primary sampling onwards), *analysis* (which will not mean anything outside the miniscule analytical volume without representativity ruling *all* mass reductions involved, also in the laboratory) and *data analysis* (“data” do not exist in isolation of their provenance). The Total Sampling Error (TSE) is by far the dominating contribution to all analytical endeavours, often 100+ times larger than the Total Analytical Error (TAE). We present a summarizing set of only seven Sampling Unit Operations (SUOs) that fully cover all practical aspects of sampling and provides a handy “toolbox” for samplers, engineers, laboratory and scientific personnel.

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Keywords: Theory of Sampling; TOS; Sampling practice; Data analysis reliability; Sampling in chemometrics

1. Introduction

Sampling is not *my* responsibility, I analyze the *data*.

Quote from a distinguished chemometrician

Sampling is not *my* responsibility, I analyze the stuff
supplied to the laboratory.

Quote from a distinguished analytical chemist

Data analysis is often regarded as separate from chemical analysis and especially separate from the process producing the *samples*, upon which depend both chemical analysis and data analysis. But “data” do not exist in a vacuum; “data” are

not separate entities, which can be dealt with in isolation—in fact “data” do not even exist until after analysis has taken place. *Someone* always has to assume responsibility for obtaining *representative* samples prior to analysis. Without representativity in this first stage in the entire analytical chain, there is no way of ever evaluating the degree of sampling bias and sampling errors embedded in the final analytical results subjected to data analysis. It has been known for more than 50 years that the combined sampling errors typically amount to 10–100, or even as much as 100–1000 times the specific analytical errors associated with the chemical analytical step itself [1], but this fact has not received the attention it deserves within chemometrics. The focus of this paper is, therefore, on the intricate task of *sharing the responsibility* for sampling, chemical analysis and data analysis/chemometrics.

Chemometricians rightly pride themselves of a holistic approach, for example, pointing out that it is often the same

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person who analyses the samples chemically and performs chemometric data analysis afterwards; it is emphasized that it is the chemometrician's job also to be involved in the planning of experimental designs before analysis. Design of optimal sampling plans can also be viewed as a special case of experimental design and, consequently, the methods TOS provides should also be an essential part of any chemometrician's toolbox.

While it clearly will be unrealistic that the same person *always* carries out sampling, chemical analysis and data analysis, this paper nevertheless aims at giving a first understanding of the severe *consequences* of not paying enough attention to representative sampling. Upon reflection, it will be seen that the consequences of perpetuating a policy of "non-involvement" almost always result in fatal consequences. It will be far the easiest for everybody involved simply to learn just enough about the Theory of Sampling to be able to state the *minimum demands* necessary to assess the nature and magnitude of whatever sampling errors have been incurred in any preceding sampling operation. In every concrete situation, it is ultimately the Principal Investigator's (PI) responsibility to see to this—or the process engineer, the quality assurance officer, etc.

Fundamentally the problem is that currently courses on sampling are taught only in very few universities. Without basic training and knowledge on the essence of the sampling theory, it is difficult (or even impossible) to obtain truly representative samples, especially when sampling heterogeneous particulate materials.

A fully developed TOS, dealing with all aspects of representative sampling exists—and has done so for 25–50 years in gradually more developed and comprehensive forms. This knowledge base should be incorporated into all relevant scientific and technological educations as a mandatory curriculum subject. Process engineering, analytical chemistry and process chemometrics, to name but a few disciplines, are clearly in need of TOS. Simply speaking, TOS shifts the focus from the *fallacy* of looking upon sampling as a mere materials handling matter, towards a scientific, quantifiable and well-documented process of exactly *how to* obtain representative samples, providing a scientific approach for getting a fixture on the sample mass, M_S commensurate with the heterogeneity of the material to be sampled. Only representative samples in this context will ensure that the conclusions from the chemical analysis and subsequent data analysis will be *reliable*.

2. The Theory of Sampling—TOS

In 1950, Pierre Gy began developing what is today known as the *Theory of Sampling* (TOS). The theory has thus been more than 50 years under way, and has today reached the level of being a complete scientific theory: It

covers all aspects of particulate sampling, ranging from the origin of seven types of sampling errors, via principles of *sampling correctness*, to a long line of physical sampling procedures and practices essential for everybody doing practical sampling, or working with sampling procedure development/optimization. The most important conclusions that can be drawn from TOS are the following.

It is *not* possible to ascertain whether a particular sample is representative from any kind of inspection or characterization of the sample *itself*. Only a full qualification of the sampling *process* can lead to recognition of representative samples. TOS states as a very useful distinction up front: "Correct samples" (truly representative samples) *only* originate from a qualified sampling process, in contrast to "incorrect samples"—which are all samples that cannot be documented to be representative in the above fashion. Such principally questionable samples may be termed "*specimens*". Specimens are worthless in the context of particulate sampling, as one is in principle unable to even assess the magnitude of sampling errors present; neither is there any way to compensate for these errors anywhere in the ensuing analytical process.

Apparently worse: Any sampling process will itself generate sampling errors. The only way to be able to eliminate, or to reduce these errors to an acceptable level, is to be able to understand *how* these sampling errors originate and are propagated.

TOS combines the technical part of sampling (i.e., to cut and correctly extract the sample) and the statistical part (to characterize the heterogeneity of the sampling target, to estimate the uncertainty generated by sampling operations and to generalize the results).

2.1. Basic definitions and terms

To understand the most important implications of TOS, a minimum knowledge of the terms and notations involved is essential. A short description of the main definitions to be used is given below [1–3].

The *lot* is the sampling target, by definition all the original material being subject to sampling, i.e., a stockpile, a process stream, a barrel, a lorry load, a train wagon, or a plot in the field, in the forest etc. The term sometimes also denotes the physical form of the material.

A *sample* is defined as the amount of correctly extracted material from the lot.

A *specimen* is produced by a non-correct selection process and is structurally biased.

An *increment* is defined as a partial sample unit that, *when combined* with other sub-samples, provides a final sample. This procedure is known as *composite sampling*.

A *fragment* is defined as the smallest physically separable particle in the lot. Fragments can be, e.g., molecules, minerals, grains (of fragments hereof), etc.

A *Group* defines a number of spatially correlated or spatially coherent fragment associations, which acts as an independent unit during sampling operations. The group sizes depend on the sampling process or procedure itself. A group will many times be identical with the ensemble of fragments present in the sample (or increment) volume (of mass M_S); in practical sampling terms a group usually denotes the material occupying the extracted volume in the sampling tool.

Increments can be a single fragment, or a single or several groups of fragments, etc. depending on the size and shape of the extraction device (the sampling tool), that altogether form a sample when combined (i.e., composite sampling). Increments would also be the term specifying, e.g., cross-stream samples from a one-dimensional moving product stream, from an elongated 1-D lot, etc. In many ways, a first understanding of *process sampling* can be understood as a series of juxtaposed ordinary increments (more on process sampling below).

Critical component is the component of interest, e.g., the chemical component analyzed for, or the *analyte*.

The *grade* of the critical component is the ratio (mass or otherwise) of the analyte to the total mass (matrix+analyte). The grades of the sample and the lot are defined as

$$a_S = \text{mass of analyte in sample / total sample mass,} \\ a_L = \text{mass of analyte in lot / total lot mass.}$$

The relative *sampling error* is defined as:

$$e = \frac{a_S - a_L}{a_L}.$$

It is emphasized that e is a *relative error* representing sample grade deviation as a proportion of true lot grade.

A selection, a sampling process, is *accurate* if the mean of e , m_e , is less than a given number, m_0 , i.e., $m_e^2 \leq m_0^2$.

A selection is *reproducible* if the variance of e , s_e^2 , is less than a given number s_0^2 , i.e., $s_e^2 \leq s_0^2$.

A selection is *representative* if the mean square (a function of both the mean as well as the variance)

$$(r_e^2 = m_e^2 + s_e^2) \leq (r_0^2 = m_0^2 + s_0^2). \quad (1)$$

Therefore, a sample is *representative* only if it is selected in a representative way or when the sampling process is both accurate and reproducible.

2.2. Lot dimensionality

To understand and use TOS, one needs first a clear understanding of the *geometry* of the lot to be sampled in relation to the Fundamental Sampling Principle (FSP—definition below). The dimensionality of a lot depends on how the sample is cut from it, and it can be any

dimension between zero and three. Lot geometries correspond more to a theoretical mathematical concept, than to the direct physical dimensions—to be fully exemplified.

From the sampling point of view, a lot can be regarded zero-dimensional on two conditions: (1) the whole lot is taken as sample, (2) or the expectance value of a sample is independent on the location of the lot where it is taken, i.e., there is *no intrinsic autocorrelation* (spatially, physically or chronologically) between the individual groups forming the lot. If the first condition is met, the sampling error is also zero. The second condition can be met if the lot can be completely mixed before sampling—at least in principle—so that the particles containing the analyte are homogeneously distributed in the volume occupied by the material forming the lot. In this case, the Fundamental Sampling Error, which for a given material depends on the sample size M_S , determines the Total Sampling Error of a correct sampling procedure. Usually only relatively small amounts of material (especially solid particulate materials including suspended solids) can be mixed close to an ideal mixture before the sampling takes place.

One-dimensional lots on the other hand consist of strings of fragments or groups, process streams or physical bodies that show a distinct *autocorrelation*. In this case, the extracted samples have to cover the two transverse dimensions of the lot completely. Two-dimensional lots have the basic layout of a plane with a finite but much smaller thickness, and here the extracted samples have to cover the entire third dimension of the lot. A case in point: Bags of sugar from a production line still represent a one-dimensional lot if each bag is retaining its production identification (time, ID-tag, etc.) even when geographically distributed across a set of two-dimensional (city, regional, national) grocery stores, etc.

Three-dimensional lots exist when the extracted samples cannot be brought to cover any of the dimensions of the lot fully. Fig. 1 illustrates schematically these basic lot dimensionalities and the typical delimitation of samples in the specific cases. Fig. 2 shows a practical example of a three- and a one-dimensional lot.

There is a further physical, or geometrical *scale issue* involved in sampling. This is related to whether the average fragment size is *large* (Fig. 2) or *small* (Fig. 3) compared to the size of the sampling tool (loosely termed the *scoop size*) and the overall dimensions of the lot itself. As will become clear below, there is a need to cover many fragments in each sampling increment, but at the same time there is an opposing wish to keep the total mass of the sample as small as possible—for practical, economical and other reasons.

So far, TOS only fully covers sampling of zero- and one-dimensional lots in full. Lots of higher sampling dimensionality are in principle to be considered separately. But very often it is possible to *transform* them into a 1-D

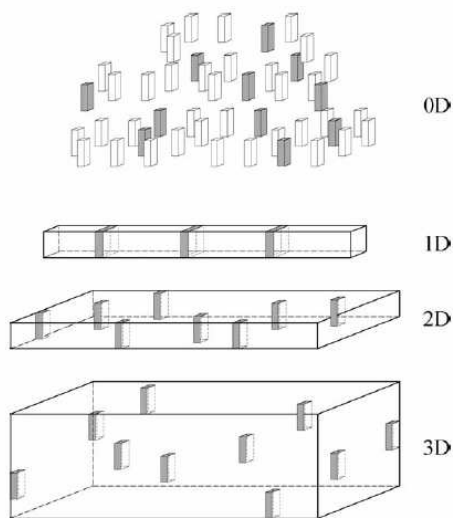


Fig. 1. Illustration of intrinsic lot dimensionality in sampling. Gray shading indicate increments to be extracted; white denotes the remaining lot material. Note that for 1-D sampling two full dimensions of the lot (height and width) must be covered by the extracted sample, while only the third full dimension (height) is covered in the 2-D case. In the 3-D case, no full dimension can be covered by the extracted samples.

configuration, or it is possible to observe a 2-D or 3-D body while it is being laid out incrementally (think of a stockpile as having been incrementally laid up by a conveyor belt, etc.). Indeed, most industrial lots did not originate in their 2-D or 3-D forms (geological and similar formations are excluded). In the summary section below, we shall give a full example of how to overcome such difficulties within the TOS realm.

There are admittedly some *generic* 2-D/3-D scenarios in which TOS at first would declare a problem, but these are special situations that have specific problem-dependent solutions, principally also using TOS. This is in fact a very challenging arena. These special cases are of no consequence for the general 0-D and 1-D sampling realm however.



Fig. 2. Illustrations of 0-D and 3-Dim. (left) and 1-Dim. lots (right) and the scale issues in lot sampling. Note the *extreme* fragment size of the lot depicted in the left panel, compared to the more conventional fragment sizes relative to the dimensions of the conveyor belt in the 1-D illustration. Lots range from these macro- to meso-scale all the way down to stockpiles of fine powders.

2.3. Sampling correctness—the Fundamental Sampling Principle

The definition of a *correct* sampling process or procedure is that [1,2,4,5]:

All fragments, or groups of fragments, or increments of the lot, must have an equal, non-zero probability of ending up in the sample, while elements foreign to the lot must have a zero probability of ending up in the sample. The increment or the sample must not be altered in any way.

Additional principles of correct sample delimitation, sample extraction and sample preparation must also be obeyed—these will be duly explained below (see Section 2.10). The total set of criteria for correctness, ensuring representative sampling is called the Fundamental Sampling Principle (FSP). A *correct* sampling process is always *accurate*, i.e., on average the effective sampling bias is zero.

In the literature, a vast catalogue of various methods for estimating “the sampling error” can be found. Most of these estimate just one of the error components presented in Gy’s theory, usually the Fundamental Sampling Error. Few methods take autocorrelation into account or distinguish between the three different sample selection strategies, random, stratified or systematic, which lead to different results in estimating the mean of the lot. If the principles of TOS regarding sampling correctness are not upheld, there is no escaping the final outcome of all such shortcut sampling attempts: incorrect samples.

What is needed to approach all sampling problems is a quantitative understanding of the concept of material heterogeneity and knowledge about the principal sampling errors that can occur, and especially *why* they occur.

2.4. First foray: overview of sampling errors

Thus, to understand the importance and impact of correct (and incorrect) sampling, one needs to have an overview of the different sources of sampling error. Systematic dealings with the totality of sampling problems over some 25 years (1950–1975) allowed Pierre Gy to



Fig. 3. Illustrative examples of *grab sampling*. Only the top and most easily accessible material has a chance of ending up in the final sample. This is by all accounts the most often used sampling procedure of all—and it is at the same time the *worst* of all sampling procedures as it blatantly ignores the Fundamental Sampling Principle FSP. TOS stresses again and again: Avoid grab sampling at all costs.

distinguish seven sampling errors. A very brief theoretical analysis of the origin of five of these is given below, with the remaining two errors only pertaining to process sampling. This analysis is needed in order to understand the origin and consequences of correct (and incorrect) sampling. While the full theoretical analysis of the sampling process in all its varied forms (processes, materials, sampling hardware, etc.) is a formidable mathematical construct (precisely because of its complete generality), it is nevertheless still possible to delineate the central tenets in a much simpler context, which is the approach chosen here. The main issue is thus to delineate just enough of the theoretical sampling analysis in order to understand the derivation of the ensuing practical sampling practices (procedures and operations).

In the original analysis, Pierre Gy labeled the total error of an analytical result “the Global Estimation Error” (GEE). This error is comprised of two fundamental contributions: The Total Analytical Error (TAE), which all chemists and other analysts are quite familiar with, and the Total Sampling Error (TSE) [1–3].

The Total Sampling Error springs from both the material properties (heterogeneity) as well as the sampling process itself. It is convenient to make this sub-division, as it emphasizes the limits to possible improvement of the results by optimizing the sampling process only (by adopting a more or less reflected or arbitrary “sampling plan”, etc). The view that the sampling process must be direct and easy-to-perform because of obvious stringent resource limitations, etc. is often encountered.

However, it is possible, indeed often recommendable, to manipulate the lot material if this is de facto necessary in order to obtain representative samples. Traditionally this is very often considered either difficult, expensive or both. Not wanting to deal properly with the heterogeneity of the lot material (not even on the conceptual level) is probably the greatest error committed in all conventional “sampling” (a more correct term would be “*specimenting*”), where emphasis almost exclusively is on obtaining a small sample as quickly as possible by the least laborious, least expensive, most direct and/or simplest procedure. This procedure has received the attribute: “Grab sampling”, an apt term. However, as shall be argued and demonstrated in extenso below, nothing good (certainly nothing *representative*) has ever come from grab

sampling: TOS displays an enormous “Hall of Shame” of the inappropriateness of all of grab sampling. Fig. 3 illustrates two examples of grab sampling from open and closed containers respectively. Neither of these examples illustrates a representative sampling process (sic).

There are two basic sampling errors encountered in all sampling operations; The Fundamental Sampling Error (FSE) and the Grouping and Segregation Error (GSE). The lot heterogeneity alone is responsible for FSE which is considered the practical minimum sampling error even when all other incorrect sampling error components have been eliminated. GSE on the other hand is related to both the sampling process and the material heterogeneity and arises from the composition and spatial distribution heterogeneity of the lot material. The magnitude of GSE also depends on the sampling process itself, especially the sampling mass.

Three further sources of error are attributed to the sampling process. These are the Increment Delimitation Error (IDE), the Increment Extraction Error (IEE) and the Increment Preparation Error (IPE), and are labeled the Incorrect Sampling Errors (ISE). All these errors are explained below. Fig. 4 provides an overview of the different sources of error and their interrelationships.

The Total Analytical Error (TAE) is almost always under strict control in the analytical laboratory and often the

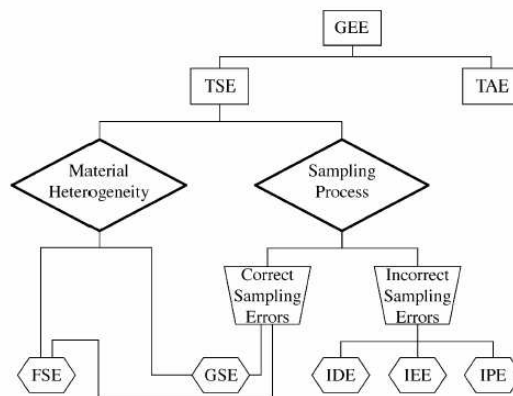


Fig. 4. First overview of the sampling errors involved in 0-D and 1-D sampling. All parts of the figure are explained fully in text.

analytical quality control concentrates on this last step of the measurement process. As the tendency of modern instruments goes towards smaller and smaller analytical volumes, this translates directly into more and more difficult representativity problems as M_S continues to shrink, in comparison to M_L . Most unfortunately (dependent on the point of view), TSE is often 10–100 or even 100–1000 times larger than the Total Analytical Error (TAE) and, consequently, efforts to minimize analytical errors do not increase the reliability of the whole measurement process—they just add the cost of the determination. TAE will not be dealt with further in this text. The mathematical formula for the Global Estimation Error (GEE) can be stated:

$$\text{GEE} = \text{TSE} + \text{TAE} \quad (2)$$

TSE can be split into two contributions, one stemming from the material itself and the errors generated by the sampling process:

$$\text{TSE} = \sum [\text{Material Heterogeneity Errors}] + \sum [\text{Sampling Process Errors}] \quad (3)$$

This is a convenient split since the first contribution cannot be tampered with directly without some intervention/work/resource expenditure—while the latter can. This first distinction opens up for the possibility of improving the quality of sampling through understanding and respecting the principles of TOS, which focuses equally on both sets of these errors.

To understand *why* we have sampling errors at all, we need to start by focusing on *material heterogeneity*. Pierre Gy states: “Heterogeneity is seen as the sole source of all sampling errors” ([1], p. 28).

2.5. Material heterogeneity

All materials making up our physical world are *heterogeneous*. The theoretical absence of heterogeneity is denoted “homogenous”, but this is a theoretical limit which is never reached in sampling. No matter how hard we try, a material is never *strictly* homogeneous [1–3,6–10].

This statement is more easily accepted than would perhaps at first be thought. For any material consisting of particles of different types, consider a *complete* replication analysis of, say, 8 or 10 repeated samplings and subsequent analysis (one is to replicate *all* sampling, sample preparation and laboratory subdivision stages etc.—absolutely not only the analytical stage). Due to random variation, there is in general no chance whatsoever that such complete replication analysis will come up with identical results. One can further refine this argument to include how the replication result is critically dependent on the scale of observation, as well as the relative sizes of the fragment

distribution versus the sampling mass. In fact this simple replication scheme, when properly designed, is the most practical and cost-effective way to quantify the *effective* heterogeneity of all kinds of material. It is seldom used in today’s laboratories, however.

An increase in the primary sample volume/mass leads to more representative samples. While this is generally true—there is at the same time an acute upper limit for the sample mass required for analysis. Development in modern analytical chemistry has as its material basis an ever decreasing analytical volume. The analytical results pertain to an ever smaller volume, but these results are nevertheless purported to be representative of the entire lot. Thus, there is a real conflict of interest between primary sampling representativity (M_S versus M_L) and the instrumental analytical volume requirement, M_{anal} , which is often of nearly insignificant size in this context (Fig. 5). If representative sampling is to have any chance at all, one would be well advised to stop thinking of the direct sample, and to adopt a multi-stage approach towards the enormous mass reductions that obviously are necessary in the chain:

$$(M_L) \rightarrow (M_S) \rightarrow (M_{\text{anal}}).$$

One cannot simultaneously stipulate primacy for *both* large and small sample volume/mass—but with TOS this conflict can be resolved: by means of multi-stage sampling and representative mass reduction.

Heterogeneity is split into two parts: Constitution Heterogeneity (CH) and Distribution Heterogeneity (DH) [1,2,3]. CH is only dependent on the composition of the



Fig. 5. What is the optimal relationship between primary sample size and the analytical sample volume (insert) and how can it come about? When sample size increases one can intuitively understand that the sample becomes more representative. But at the same time, today’s analytical volumes continue to decrease (insert) as the analytical instruments become more and more precise. For all heterogeneous materials, there is consequently an intrinsic contradiction between primary sampling representativity and the instrumental analytical volume requirements. This is the root cause of all sampling and representativity issues.



Fig. 6. Identical material composition with alternative physical grain-size states. Comminution (crushing) reduces the average grain-size, thus making it very much easier to mix and homogenize the material with a resulting significant reduction in constitutional heterogeneity. Blended coffees offer a vivid illustration.

material while DH is dependent on the physical, spatial distribution of the critical component in the lot/sample.

2.5.1. Constitution Heterogeneity, CH

CH is inherently dependent on the composition, shape, size, density etc. of the particles or fragments making up the lot. If a great overall composition-wise difference between the individual fragments exists, the constitution heterogeneity is large, but if the fragments are more homogeneous CH is lower. The total contribution to heterogeneity is never nil, however, as that would be the case of all fragments being strictly identical. Mixing and blending does not change CH. The *only* way to alter the constitution heterogeneity of any given material would be by crushing (comminution—Fig. 6) or by other methods changing the physical properties of a sample. The reduction of the average grain-size is the dominating factor in reducing CH by such means.

2.5.2. Distribution Heterogeneity

DH is dependent on the physical, spatial distribution of the fragments of the lot, on certain aspects of the method of sample extraction, and finally on CH. The degree of DH is limited by CH of the lot. For the sake of illustration, imagine a lot consisting of black and white spheres and with significantly different grain-size distributions. If all the black spheres are to be found at the bottom of the lot and the

white spheres are more to the top, the system displays a very high DH. If on the other hand the spheres were to be well mixed (“homogenized”), the system DH would be significantly reduced. The size of extracted groups of fragments (increments) has great influence on DH. As an ideal end-member case if the increments consist of only one fragment, DH would be zero. An increasing number of fragments in the groups consequently implies an increase in DH. Fragment size and density also influence DH. For example, particles with large differences in size (and/or density) tend to segregate or stratify heavily, with the smallest and/or densest particles at the bottom of the lot.

The effective sampling error resulting from DH can be split conceptually into two factors according to the arguments presented above: a *grouping factor* (Y) and a *segregation factor* (Z). The grouping factor is a measure of the total number of fragments in the lot (N_F) to the number of groups (N_G), more precisely:

$$Y = \frac{N_F - N_G}{N_G - 1} \text{ which is well approximated by:}$$

$$Y = \frac{N_F}{N_G} \quad (4)$$

From this, it is seen that the grouping factor, Y , is but a quantitative expression of the lot in terms of a collection of Y virtual samples, all of size N_G .

The segregation factor, Z , cannot be easily defined mathematically [1], but is very easily illustrated as a measure of the extent of the local and global *segregation* and/or *stratification* in the lot, clearly illustrated in Figs. 7 and 9.

The *interconnection* of DH and CH can be written as [1–3]:

$$DH = \frac{1 + YZ}{1 + Y} CH. \quad (5)$$

A Venn diagram of this interconnection between DH and CH (for any given lot which does not undergo comminution) can be seen in Fig. 8.

Contemplation of these two intrinsic heterogeneity factors Y and Z only plays a role in the qualitative, theoretical formulation of TOS. By careful choices of their mathematical definitions, Pierre Gy was able to end up with



Fig. 7. Illustration of rapidly decreasing GSE as a consequence of progressive mixing (left to right). Note identical material composition in all panels, i.e., CH=constant, while DH (manifesting the *local* stratification/segregation) decreases significantly. A single sample of constant mass/volume, selected from the rightmost state will of course be immensely more representative for the whole lot than any taken from either of the less mixed material states.

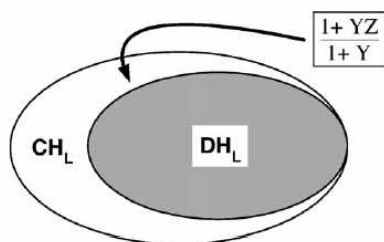


Fig. 8. Venn-diagram of the relationship between CH_L and DH_L . Y is the grouping factor and Z is the segregation factor. Extensive theoretical TOS-derivations lead to this elegant formula.

conceptually simple yet extremely powerful derivations for the relationships between the various sampling errors and the sampling process characteristics—the end result of which we have been able to express as seven Sampling Unit Operations (SUOs) below. The seven SUO are sufficient to address *all* sampling problems.

2.6. The Grouping and Segregation Error (GSE)

The Grouping and Segregation Error (GSE) is a practically unavoidable error in any sampling. GSE is a result of both the material heterogeneity and the sampling process itself. This error arises as soon as the sampling increments are not ideal, i.e., when we do not sample fragments one by one and with equal probability of being selected (FSP). All practical sampling increments do in fact contain thousands to millions or more of fragments depending on the grain-sizes involved. This ensures that all fragments do *not* have the same probability of being selected; i.e., when one specific fragment is extracted, neighboring fragments are bound to be extracted too. Often some significant local correlation between neighboring fragments exists. This correlation can be induced by external or internal physical agents, as for instance gravity producing segregation or by incomplete mixing due to differential grain surface properties (“stickiness”, etc), thus violating the principle of extracting fragments completely at random from the entire lot. GSE decreases as the size of the selected groups decreases and reaches its limit when individual fragments are selected to form the sample.

Thus, GSE depends primarily on the local level of fragment segregation, which in turn depends strongly on the material differences in particle size, shape and density. Segregation almost always occurs when dealing with particulate materials, both stationary and in motion. One prudent rule of thumb would therefore be: to *always* mix thoroughly before any further subdivision of any material lot (of manageable proportions). Many experiments and investigations have clearly shown that the presence of a significant residual heterogeneity is the overwhelming rule, rather than the exception. There is often a serious underestimation of the degree of

homogenization obtainable by conventional means, and often a significantly longer mixing time is needed than what is commonly held, in order to make serious reductions in GSE.

GSE can only be *minimized* by extensive mixing or blending, but almost never completely. Mixing in and of itself is no guarantee for minimum GSE. Many materials will always display an innate propensity for segregation, even immediately after mixing, e.g., highly density-fractionated materials, suspensions. Such systems require constant monitoring and treatment, but once this feature has been duly recognized it can always be dealt with satisfactorily.

An ideally mixed material would give a minimum GSE, characterizing the lowest possible residual heterogeneity. Materials treated thus are called *uniform materials*, for which special, less difficult sampling situations hold [11,12]. However, this is of course only provided these systems do not revert to segregated states after minimization of GSE.

It is not possible to determine GSE directly, but it can be found by experimentally determining the Fundamental Sampling Error (FSE) and the Total Sampling Error (TSE). Then—presuming all other errors are eliminated or non-existing (only sampling *correctness* will guarantee this)—one can calculate GSE from: $TSE = GSE + FSE$.

To summarize: GSE comprises two error sources: grouping and segregation. The contribution from (local) grouping can be minimized by decreasing, as far as possible or feasible, the size of the increments—with the ensuing mandate to use (very) many increments to make up the sample (Fig. 9 illustrates this). The contribution from segregation can be minimized by thorough mixing or blending of the lot material before primary sampling, if this is possible; if not, composite sampling is our only course of action (see further below), preferably by using systematic or stratified sample selection schemes. Mixing of the primary sample material before secondary sampling is equally important and this mandate holds for all further sampling stages.

2.7. The errors of the sampling process

During the process of sampling, a number of errors can be highly influential on the Total Sampling Error if not properly recognized and countered. These errors are categorized as *correct* and *incorrect* sampling errors, respectively. The correct errors are comprised by the Fundamental Sampling Error (FSE) and the Grouping and Segregation Error (GSE), and are *unavoidable*, while the incorrect errors are introduced *if, and when*, the principles of correct sampling are not obeyed.

However, the incorrect errors can be completely eliminated—or at least be reduced (to being negligible) simply by following the guidelines for *correct* sampling, given in TOS. All these errors are treated comprehensively below.

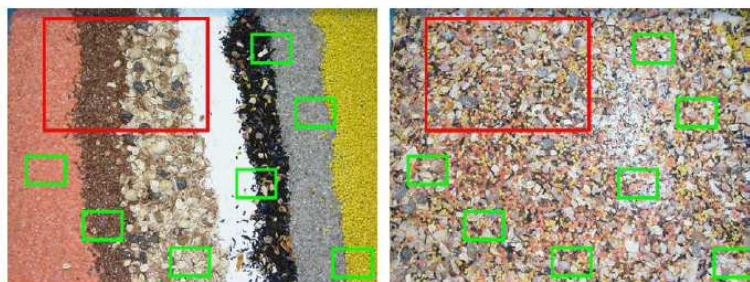


Fig. 9. Illustration of the effects of *mixing* and *composite sampling*. Left panel: thoroughly segregated material. Right panel: the same material mixed to a much lower residual heterogeneity state. For both situations (panels), it may be appreciated how *compositing* a number of small samples gives a much more representative sample than extracting only one large sample of the same mass/volume. Even in the lower heterogeneity state, one still gains in representativity by composite sampling. GSE is also lowered significantly even if one was forced to use only one large sample size (large rectangle in both panels).

2.8. The Fundamental Sampling Error

The Fundamental Sampling Error (FSE), introduced above, is inherent to the material properties (size, shape, density, composition amongst other). For a given state of the lot (particle size, density, etc.), the contribution from FSE is constant and cannot be altered. The only way to do this is to *physically* improve the lot characteristics so that better, i.e., more representative sampling can be obtained. The most often encountered method is to comminute the particles to a smaller particle size. FSE will *always* be lower for a smaller particle size.

Only in two very special and often unachievable situations, will FSE be strictly zero:

- The sample is the whole lot ($M_S = M_L$).
- The lot is (strictly) homogeneous.

It is of the highest value to be able to calculate FSE from a number of material parameters to get a realistic idea of the properties of the sampling procedures and especially to estimate the necessary sample sizes. It is therefore vital to be able to assess the magnitude of FSE. This holds for all sampling of particulate materials.

2.8.1. Estimation of FSE

To estimate the Fundamental Sampling Error, “Gy’s formula” (so termed by everybody else *but* the originator himself) was derived and has since proved to be of extreme usefulness for this purpose within many practical industrial and scientific applications. The formula was derived for particulate materials and only yields FSE to an order of magnitude. However, this is very often all that is needed [1,2,13–15].

$$s^2(\text{FSE}) = Cd^3 \left(\frac{1}{M_S} - \frac{1}{M_L} \right) \approx \frac{Cd^3}{M_S} \quad [\text{“Gy’s formula”}]. \quad (6)$$

The mass of the lot, M_L almost always cancels out due to its far larger size. C , termed “the sampling constant”, is

actually short for the product of four material parameters: c , f , g , and β . d is a measure of the coarsest fragment size (top 95% retaining sieve mesh size). The specific details of the formula are explained in Appendix A.

2.8.2. Solutions of sampling problems using Gy’s formula

As mentioned above, FSE is the sampling error of a zero-dimensional lot, i.e., a lot that can be thoroughly mixed before sampling. Estimation of FSE is, therefore, a useful exercise. It can be used to assess, audit and optimize all sampling and mass reduction steps, where a thorough mixing is possible before extracting the sample, i.e., usually all sampling steps following the primary sampling. As C and d can always be estimated for (almost) any particulate material, the FSE model can be used to estimate the variance of a given sampling step (Eq. (6)), and minimum sample size M_S if the required uncertainty level (variance) is fixed (Eq. (7)).

$$M_S = \frac{Cd^3}{s_0^2(\text{FSE})} \quad (7)$$

This relationship can also be re-arranged to give the necessary particle size to which a material must be comminuted/crushed, for a given sample mass, to correspond to a desired variance of FSE:

$$d^3 = \frac{Cs_0^2(\text{FSE})}{M_S}. \quad (8)$$

Gy’s Formula is of absolutely fundamental importance in sampling. Either the sample mass, or the average grain-size, or the acceptance level of FSE can be directly estimated on this basis. The sampling constant, C , will be fixed as soon as $s_0^2(\text{FSE})$ has been determined, because all other parameters are estimated easily enough (“it just takes a little work”). Examples on the use of the FSE model can be found, e.g., in Refs. [1–3,13–16].

2.9. The incorrect sampling errors

In contrast to the correct sampling errors (CSE), the incorrect sampling errors (ISE) can all be greatly minimized,

sometimes completely eliminated by obeying the principles of *sampling correctness*.

For the analysis below, contemplate what will be the outcome of *repeated sampling*. *Why, how, and by how much* would the analytical results pertaining to repeated samplings differ quantitatively? The variance of a series of replicate samplings is a reflection of the fact that different material volumes/masses *per force* must result when performing replicate sampling because there is no option for “sampling with replacement” in the physical world. Once a particular increment or sample has been taken, this part of the material lot is gone for good, and no matter how physically close one performs the replicate sampling, the increment delineation and materialization taking place (see below) will be different to some degree. With respect to Fig. 9 above, it will be appreciated that there will *always* be a baseline replication sampling error. This will be larger or smaller depending on the material GSE and *especially* the specific sampling procedure(s) employed. The latter errors, intimately related to the correctness of the sampling procedure, are in focus below.

2.9.1. The Increment Delimitation Error (IDE)

IDE occurs when the actual shape of the extracted increment *deviates* from the correct geometrically delimited increment [1–3,17,18]. For instance, when sampling a conveyor belt, it is important that the sides of the cutting device are strictly parallel and that the cutter traverses the entire stream at *uniform* speed, resulting in an equal representation of the entire width of the belt in the final sample—this condition must be rigorously upheld for *all* increments/samples. The correct shape of the increment to be extracted is the target, and deviation from this correct shape, for replicate samplings, is the root cause of IDE. Fig. 10 (central panel) illustrates a correctly delimited and extracted increment on a stopped conveyor belt transporting coal in a power plant.

This type of complete (“stopped belt”) sampling is only used for calibration purposes. Similar operations on a

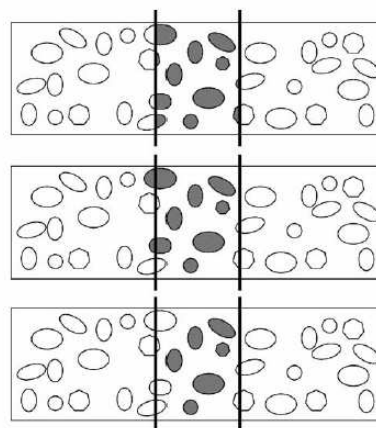


Fig. 11. Schematic illustration of fragments sampled by a cross-stream sampler, for example on a conveyor belt. Grey shadings indicate material in the final sample and white shadings are left out. Top: Correctly delimited increment. Middle: Correct practical extraction of fragments. Bottom: Incorrect extraction of fragments, since fragments belonging to the increment in fact does not end up in the sample (the opposite may take place as well). The larger the fragment size, the higher the probability that it hits the cutting edges.

moving belt using an automated sampler, if not performed with similar care, will often result in significant deviations of the actual volume delineated and extracted between repeated samples, thus contributing to *both* IDE and IEE (see immediately below).

2.9.2. The Increment Extraction Error (IEE)

When extracting the (correctly) delimited increment, but not respecting a set of practical extraction rules, the Increment Extraction Error IEE will occur [1–3,17,18]. For instance, when handling particulate matter, it is important that the center of gravity rule is obeyed. This rule states that a fragment having its center of gravity inside the delimited increment should also end up in the final sample (see Fig. 11).



Fig. 10. Illustration of IDE. In order for IDE to be fully suppressed, the cut delineation must correspond exactly with the geometrical plan, i.e., the planar sides of the cut must be parallel and all material inside the increment must be fully extracted. In the present case, coal is sampled on a stopped conveyor belt by inserting a manual “cutter-device” and scooping out *all* the material (the fine particles in the groove are extracted using a brush). (The material in the rightmost panel has fallen into the “increment space” only *after* removal of the cutter-device.)

When using a cross-stream sampler, the top edges must be designed so that a particle hitting it will in fact bounce to the right side, e.g., either in or out of the device depending on the center of gravity. It has been observed in industrial samplers that disobeying this principle can result in significant sampling errors. Other examples cover samplers functioning by vacuum in powder streams. Higher fluid flow in the sample cutter opening may result in fine particles being overrepresented and coarse particles underrepresented in the extracted sample, as the fine particles are preferentially sucked into the sample cutter opening. This also holds for, e.g., hot gas and smoke sampling, where “isokinetic sampling” is *de rigueur*.

In Fig. 11, the top panel shows what the ideal sample *should be*, while the middle panel shows how a correctly extracted sample actually *will be*. The theoretical difference between these two is a contribution to the sampling error that cannot be avoided without altering the physical state of the material. Hence, even correct sampling does not eliminate IEE, but it pulls heavily towards minimizing the contributions from ISE.

2.9.3. The Increment Preparation Error (IPE)

After the actual extraction of the sample, it may undertake a number of further steps before reaching analysis, storage or further processing. In this process, the sample may be altered by a number of factors such as: human errors, spillage, contamination, packaging, adhesion of critical component(s) to sides of containers/bags/gear, loss of fine particles (dust) during handling or crushing/comminution, moisture uptake/loss, biodegradation, etc. Also deliberate alteration of the samples, like sabotage or fraud, categorizes as preparation errors. Common for all preparation errors are the fact that it is not possible to treat them statistically [1,2]. They do not follow specific distributions.

Correct sampling is defined as the sum total of the set of these (and a few other) practical guidelines for suppressing unnecessary, indeed critically unwanted, inter-sample variations, which loosely can be described as resulting from lack of appreciation of the tenets of TOS. Correct sampling prevents the occurrence of incorrect sampling errors.

2.10. Practical sampling—seven Sampling Unit Operations

In the theoretical sampling analysis above, we have along the way highlighted various sampling handling and manipulation procedures that are specifically designed to alleviate one or more of the CSE as well as the ISE. Following from the complete analysis in TOS, we have arrived at formulating what we have termed the seven *Sampling Unit Operations* (SUO) (it has also been suggested to term these Practical Sampling Principles, PSP), which are listed below, as they constitute the total arsenal available for the sampling problems. The seven SUO are not necessarily all to be

invoked in any particular sampling problem, in many cases a problem-specific subset will suffice. Creative sub-setting of individual SUOs and an appropriate order of application define the entire sampling playing field.

- SUO 1. Always perform a heterogeneity characterization of new materials
- SUO 2. Mix (homogenize) well before all further sampling steps
- SUO 3. Use composite sampling instead of premature focus on M_S
- SUO 4. Only use representative mass reduction
- SUO 5. Comminution whenever necessary (reduction in grain size)
- SUO 6. Perform variographic characterization of 1-D heterogeneity
- SUO 7. Whenever possible turn 2-D and 3-D lots into 1-D equivalents

Of these operations, SUOs 2, 3, and 4 constitute the most frequently used everyday tools of the trade, with SUO 5 called upon whenever needed. Representative sampling is not much more than a serious interest in TOS combined with four practical Sampling Unit Operations (SUOs 2–5) and three guiding principles (SUOs 1, 6, 7).

As will be appreciated, SUOs 1 and 6 constitute the initial material heterogeneity characterization which is *only* necessary when a new sampling operation is initiated. SUO 6 is not inherent to 0-D sampling and will be dealt with accordingly elsewhere.

SUO 7 constitutes the *current frontier* of TOS. Strictly speaking, TOS only deals completely with 0-D and 1-D sampling, while all the SUOs 2–5 are also used when approaching 2-D and/or 3-D lot configurations—SUO 7 suggests one sure way to eliminate the sometimes quite overwhelming 2-D and 3-D direct sampling problems. If the lot is *too* large, SUO 7 and SUO 2 cannot be applied and other approaches may be followed.

For want of space, it cannot be the intention here to also to supply a practical sampling manual. However, a comprehensive TOS-introduction Special Issue, complete with extensive case histories and solved practical sampling cases was recently published [25], which forms the perfect companion to the present paper.

2.11. Sampling strategies

Setting up a correct sampling strategy is often both difficult and/or tedious for the uninitiated, but it will always pay off as the *only* guarantee for truly *representative* samples. The following procedure for developing a sampling strategy may be useful:

1. Always perform an initial survey of lot heterogeneity (SUO 1). It should be obvious that it is neither possible to

fix a sample mass, M_S , nor to choose a particular sampling plan without quantitative information about lot heterogeneity.

2. Use only appropriate problem-specific means (SUOs 1–7), i.e., sample correctly, to eliminate all ISE, and optimize the sampling plan simultaneously to minimize the Fundamental Sampling Error (FSE) and the Grouping and Segregation Error (GSE). In dealing with one-dimensional process streams, or time series, minimize the influence of periodic fluctuations, both long and short term (SUOs 6–7, process sampling is only mentioned very briefly in this paper).

At all sampling steps, the sampling correctness should be controlled by respecting the rules about sampling hardware and procedures provided by TOS, as this will eliminate the incorrect sampling errors, and simultaneously ensure unbiased samples. A benefit of this is that the general sampling variances will also be reduced [1,2]. The choice of exactly which mechanical sampler or procedure to use is always dependent on the material to be sampled and rests heavily on experience, etc. Slurries, liquids and dusty gases need different equipment from particulate solids, but the principles are the same. For more information on the different *correct devices and methods* for sampling different materials and media, the reader is referred to the extensive literature [1–9,12,18].

2.12. After primary sampling?

The above exposé mainly focuses on showing the theory and principles behind, and the practical procedures for correct and variance minimized—hence representative—hence reliable primary sampling. What happens next?—What happens when a representative primary sample is sent to the laboratory? Easy! TOS, as delineated above, also governs the secondary, tertiary... sampling steps in the laboratory. The only thing which changes is the *scale* at which the pertinent SUOs operate. All problem-relevant practical SUOs are identical at the hierarchically lower scale-levels (only the dimensions of the hardware equipment changes, as does the masses involved, etc.). Once the essential TOS is mastered, its principles can, indeed should, simply be applied at all appropriate scales—until the final, representative analytical mass (volume) has been arrived at.

2.13. The special case of one-dimensional sampling

Conveyor belts or pipelines, tubes, etc., transporting material can be considered one-dimensional lots. When sampling this type of lot, special attention should be paid to the rules and principles pertaining to autocorrelated process or product streams, which are thoroughly described in TOS under the heading of 1-D process sampling. A special tool for analysis of periodic trends, the *variogram*, is provided, along with a number of specific 1-D sampling principles.

Two more sampling errors are introduced, related to short- and long-range fluctuations, respectively. The local “random noise” error component is also present in 1-D sampling; however, this can be shown to be equivalent to FSE+GSE, just as in the 0-Dim case. TOS also provides in-depth description of a vast array of automated 1-D samplers, the design and operation of these, along with instructions on frequency, etc. of sub-sample extraction. The reader is referred to the TOS literature [1–3,17–21] on 1-D sampling for further details.

3. Focus on correct mass reduction

To illustrate the most important sampling phenomena and principles from a distinct practical point of view, we provide a brief focus on the critical issue of mass reduction (SUO 4). Whether because of the wish for a *large* primary sample or in order for the powerful SUO 3: *composite sampling* to be used for its fullest design purpose, unavoidably one is sooner or later likely to end up with a sample mass which, although more representative than any alternative, is bound to be much larger than the minimum sample mass, M_S , and substantially larger than that needed for analysis (M_{anal}). Thus, the critical need for reliable, i.e., *representative mass reduction* tools both in the primary, secondary and also in higher sampling stages. Availability of such tools would allow the freedom to concentrate on methodology to obtain representative samples in the first place, knowing that the representative nature of the sample will be preserved during the process of mass reduction.

3.1. The critical role of a correct mass reduction device/method

Representative sampling is in itself a mass reduction step—but the reverse is most emphatically not true: it is very seldom, if indeed ever, the case that an indiscriminate focus only on the quantitative mass reduction aspect leads to correct and representative sampling results [1,2,3]. The primary sampling stage itself is always the most dominant mass reduction step in the entire sampling-and-analysis chain, and we often need to further reduce the size or mass of our primary sample. This is traditionally most often done by one of the following methods:

- Scoop extraction of a small amount from the top of a container/bag/beaker/bin/box (*non-TOS*), e.g., Figs. 3 and 5.
- More sophisticated scooping methods (alas all *per force* only variations on a bad theme (*non-TOS*)).
- Using specially designed mass reduction devices, methods or procedures (*TOS-compatible or non-TOS*).

To the uninitiated, this issue often only seems to be an unimportant materials handling step that simply provides a

final sub-sample mass for analysis. This is a most dangerous and very unfortunate misunderstanding. The following will clearly illustrate the paramount importance of careful consideration when choosing a method or device for sample mass reduction [22,23].

A large experimental series has been carried out to investigate the reliability of 17 current methods for mass reduction. A three-component lot of 2000 g was reduced in all experiments. The aim of this extensive survey was to assess and rank—with regard to representativity—all the currently used methods for mass reduction available in the international sampling, analytical and industrial-academic realms. Only a brief summary of the salient results from this study is presented below; this study is reported in full in Ref. [24].

3.1.1. Methods for mass reduction

A complete set of all current methods and devices in use today for mass reduction (see Fig. 12 for some examples) were investigated in detail and compared. These are:

- *Grab sampling*. Obtaining the sample by simply scooping from the top of the lot. This method is the most often used method in practice.
- *Alternate shoveling*. The mass is reduced by shoveling the material into two piles in an alternating fashion. One pile is then randomly chosen and subsequently shoveled into two new smaller piles and so forth.
- *Fractional shoveling*. Analog to alternate shoveling, but using (in this case) five piles instead of two.

- *“Spoon method”*. A method used in official seed testing. The lot material is spread in an “S” like pattern layer by layer into a flat container. Afterwards five sub-samples are extracted by inserting a sharp spatula and extracting all the way to the bottom by a small square scoop. The five sub-samples are combined to yield the final composite sample.
- *Riffle splitters (eight different versions)*. Riffle splitters come in a wide variety, some more correct than others. They are all operated pouring the material over a number of chutes, every other leading to two different recipient reservoirs. The number and width of chutes vary between models.
- *Rotational splitters (three different versions)*. Rotational dividers basically consist of a rotating nozzle pouring the sample over a number of radial chutes. In some models, the chute width is variable. In the present experimental series, two overall models were tested: a divider with 32 chutes leading to each their reservoir and an 8 chute model with computer controlled variable chute width. Rotational splitters are dynamically equivalent to riffle splitters. It is possible to obtain a significantly higher number of chutes with rotational splitters, at the expense of some versatility in use.
- *Other methods*. A so-called “Boemer divider” was also tested (operated in two different ways). It basically consists of a central cone over which the sample is poured, dividing it across 38 radially distributed chutes. Every second chute also leads to one of two accumulating reservoirs.



Fig. 12. Examples of mass reduction methods and devices. Top left: Spoon method (pouring); Top middle: Fractional shoveling; Top right: Boemer divider; Bottom left: Schematic of the “Vario divider”; Bottom middle and bottom right: A 10-chute and a 34-chute riffle splitter.

3.1.2. Experimental procedure

A composite material was designed to simulate difficult, natural sampling materials and conditions. It was required that the material system should include small, intermediate and large particles to ensure a significant segregation propensity, and that one of the components must be prone to bouncing, with clear differences in density. The material finally chosen was composed of:

- 0.10% w/w glass spheres (diameter 1 mm)
- 10.00% w/w rape seed (diameter 2–3 mm bouncing)
- 89.90% w/w wheat seeds (diameter 3–6 mm)

A 2000-g lot was thoroughly mixed at the start of all experiments and reduced by one of the above-mentioned methods to either 100 or 125 g, respectively. All final sub-samples were separated into their constituents by sieving and the individual fractions were weighed. The experiments were repeated 20 times, in two blocks of ten performed by two different operators resulting in very stable and reliable summary statistics.

3.1.3. Results and conclusions

To illustrate the reliability of the methods and devices tested, we here only present the final results for the overall *representativeness* (Fig. 13), i.e., the combined measure of both accuracy and precision pooled over all three constituents. This measure is the most comprehensive representativity characteristic which can be envisioned. Given that the material used in all comparative experiments successfully mimics many types of “difficult”

particulate materials (the present designed material represents a particularly demanding material with widely contrasting characteristics for the three components), these results are rather generic with regard to device type performance etc. This is further elaborated in Ref. [24].

Fig. 13 provides a complete overview of representativeness pooled for wheat, rape seed and glass, thus representing and covering all principal concentration levels: trace, intermediate, major components (spanning 0.1% w/w to 89.9% w/w). Fig. 13 presents an *overall* measure of method or device reliability for the purpose of representative mass reduction.

The following (major) conclusions can be drawn [24]:

- Grab sampling is the by far worst performer of all! Shoveling methods in general also provide unreliable biased results.
- Riffle splitters generally provide most reliable and excellent representativities.
 - The larger the number of chutes, the smaller the bias.
 - Closed riffle splitters provide better results than open models (open models loose significant amounts of bouncing material).
- Rotational dividers provide equally reliable mass reduction. They also require very little maintenance and are fast to use. Set-back would appear to be difficulty to cleaning sticky materials and immobility when needed in field work.
- The Boerner divider, if used properly, provides the marginally most accurate and precise overall mass

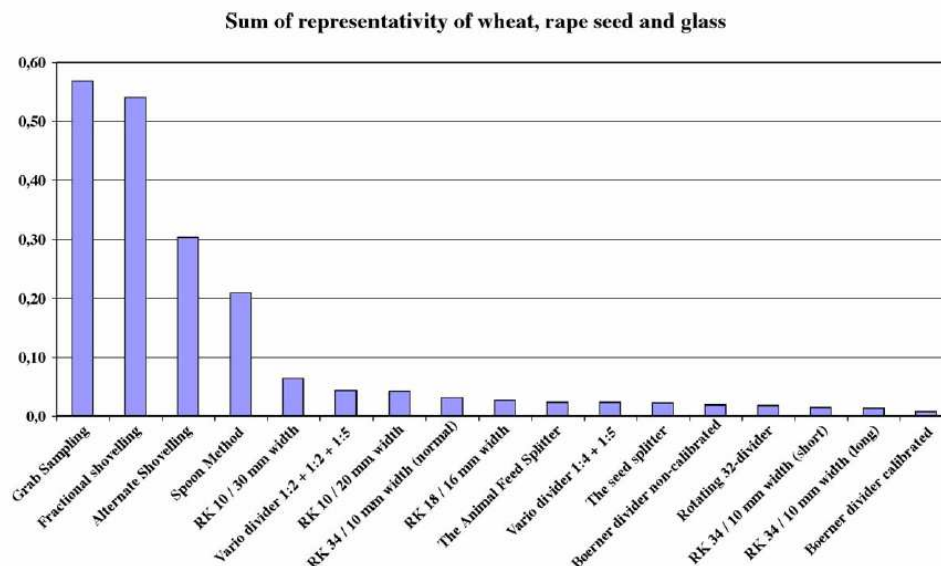


Fig. 13. Pooled representativeness (wheat, rape seed and glass). Representativeness should be as low as possible, cf. Eq. (1) above. Higher sums thus mean lower reliability ($r_e^2 = m_e^2 + s_e^2$).

reduction with a very narrow replicate distribution, but probably only for this particular material as the Boerner divider actually was *designed* for grain splitting purposes.

When choosing a specific method for mass reduction, either in the field or in the laboratory, reliability and representativity (accuracy and reproducibility) of final sub-samples is the primary focus. Grab sampling (and shoveling methods) is to be totally avoided—even though this is by far the most used method today! There are plenty of alternatives: Most laboratories can easily procure miniature riffle splitters when dealing with powders or other particulate materials, e.g., pharmaceutical mixtures for quality control. This is the best way to perform final sub-sampling for extraction, solution or whatever analytical preparation needed as in TOS. This will greatly improve the quality of laboratory work.

Extraction of the primary sample is, as always, a totally separate matter, and may at times be difficult. More attention should be paid to both these sampling aspects.

4. Discussion—a summary illustration

A generic illustration is presented below intended to shed light on most of the principal practical sampling issues delineated above. It is not a complete practical account, but rather a qualitative overview of which relevant SUOs that may be brought to bear on a difficult sampling issue, and their interrelationships. The specific details of all sampling problems are always very much problem-dependent.

At first sight perhaps, a simple scenario, yet a very difficult sampling problem, would be that of a container full of, say, waste material, organic produce, rocks or construction materials, where only the top would appear to be readily accessible. Here we shall illustrate by way of a container topped off with waste material from a recent building rejuvenation project, Fig. 14. It was found, however, that parts of the defunct building materials had been treated thoroughly with a particular tar impregnate (which had been in extensive use some 75 years ago), which by modern environmental standards was now found to contain several toxic PAH-compounds on the exclusion list of the authorities responsible for testing and accepting recycled building materials. The question soon emerged: “Is the *average concentration* of these analytes (together with several others) in this container contaminated to a level above, or below, the particular official threshold?” This job then fell to the *professional sampler*, who was to deliver a representative sample from this container load ultimately of the order of only 2 g (for GC-MS and other analytical modalities).

Without TOS training, most chemical and data analysts would agree that primary sampling of such heterogeneous



Fig. 14. Construction materials meant for recycling, but partly contaminated by PAH from earlier tar impregnation. Insert shows an example of this most difficult lot heterogeneity manifestation. Even such “impossible-to-sample” problems are *doable* in the context of TOS however, see text.

material presents a very difficult task indeed. However, materials of comparable heterogeneity as the one illustrated are universally met for everyday analysis in many industrial monitoring and scientific contexts.

How to solve this singularly nontrivial sampling problem?

For TOS, there is no problem as such—“there is just a little work”. But in order to obtain the sought for *representative* sample, it is necessary to do the work needed. To sample this type of composite lot correctly, there will be only one option (as composite sampling alone clearly will not do for this poly-modal, extremely heterogeneous material): One has to *transfer* the entire lot to similar empty container, for example by a small front-loader, and use either scoopfuls the size of the individual front-loads, or other similar full cross-stream samples, as *discrete increments* from this one-dimensional stream. Again the container depicted did not come into existence in its present form; it was specifically laid up *incrementally*, so the whole sampling problem *could* alternatively, and much more simply, have been eliminated already when the container load was being laid up, *had* proper knowledge of TOS’ principles been at hand. But the problem as stated now has to be solved nevertheless. Here’s how:

As soon as a reasonable primary sampling rate has been decided for the 3-D→1-D sampling scheme indicated (SUO 7), it is patently obvious that *comminution* of the average particle size is critically needed (SUO 5); there will be more than one size reduction step in this particular case, each followed by thorough homogenization before mass reduction. This primary sample mass, which in this case will be large, first has to be crushed down to a suitably small grain-size, for example by a readily available standard laboratory jaw-crusher (or similar) and then thoroughly mixed, after which a static riffle-splitter may

be used to extract the next sub-sample, initiating a new series of crushing, homogenization and splitting. This staged process is to be continued until the final mass needed for analysis, M_{anal} , is achieved. “The *necessary* work *must* be carried out”—what this means in this particular case would, e.g., be that a set of riffle splitters at appropriately matching particle size ranges are indeed available, and so on).

The point here is that the severe heterogeneity and the impracticality of the nature of the lot material *necessitates* that TOS be used to design the needed sampling protocol, primary sampling should *not* be taken directly from this 3-D lot, but from the transformed 3-D→1-D relocation process. After that, comminution is clearly an imperative. Once the primary sample mass has been brought down to a manageable grain-size regime, however, the remaining mass reduction steps are much more easily performed in turn. This particular job simply invoked SUOs 7, 3, 5, and 4 in this order.

Other realizations of the illustrated 3-D→1-D transformation scheme could, e.g., involve installing automatic samplers. This is preferably done for conveyor belts or in pipelines. In this way, the “impossibility” of sampling large heaps, stockpiles or similar storage means correctly can nearly always be circumvented within the confines of creative application of TOS.

There are no impossible sampling problems—there are only situations, which are judged, often hastily and quite unscientifically, to be either too impractical or too costly!

5. Conclusions

Based on the exposition of TOS and the presented illustrations, the following conclusions are drawn:

- It is important to know, at least to a certain level, the basic principles and practice of TOS when dealing with sampling of heterogeneous materials.
- Respecting the relevant *correct* TOS principles is a guarantee for arriving at unbiased samples concomitant with the lowest possible Total Sampling Error.
- FSE can *only* be reduced by comminution (crushing).
- Mixing minimizes the grouping contribution to GSE significantly.
- Decreasing increment size minimizes the segregation contribution to GSE.
- Composite sampling is powerful for primary sampling of 0-D and 1,(2,3)-D lots.
- Careful consideration of (problem-dependent) correct mass reduction methods or devices is mandatory. The riffle-splitting *principle* (static/rotary) reigns supreme.

TOS is available at any entry level one would wish to desire. The three supreme textbooks [1–3] are all to be

recommended, although they are a distinctly different levels. Today there is sufficient academic know-how, abundant literature and courses available, worldwide at least, that no one needs to continue to be without initiation to TOS. In addition, there is ample, highly competent international consulting expertise available, first of all inside, but also outside the immediate TOS-domain, e.g., see also the excellent overview of the technical theory and practical application of TOS in [26] from the geostatistical community.

Acknowledgements

We thank Pierre Gy, *octogenarian July 25, 2004*, for his monumental achievements: founding, developing, educating, consulting, inspiring... all and everybody about TOS. His intellectual honesty is a continuing inspiration for all of us at ACABS and at LUT.

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We are grateful for the comments of two thorough reviewers, one chemometrician and one geostatistician, who provided numerous valuable and constructive criticisms.

Appendix A

A short introductory description of the full set of parameters in the “Gy formula”:

- c is termed the “constitutional parameter” (dimensionless) of specific gravity expressed in g/cm^3 . It is mathematically defined and can vary from a fraction of unity to several million. The constitution parameter can be calculated from the following formula:

$$c = \frac{\left(1 - \frac{a_L}{\alpha}\right)^2}{\frac{a_L}{\alpha}} \rho_c + \left(1 - \frac{a_L}{\alpha}\right) \rho_m$$

where: a_L is the average concentration of the lot; α is concentration of the critical particles (particles of interest); ρ_c is the density of the critical particles; ρ_m is the density of the matrix

- f is a “particle shape factor” (dimensionless) describing the deviation from the ideal shape of a square. A square will have $f=1$, a sphere $f=0.52$ and a almost flat disc $f=0.1$
- g is a “size distribution factor” (dimensionless) describing the span of particle sizes in the lot. Rules of thumb: If all particles have the same size, then $g=1$; if $1 < d/d_{0.05} < 2$ then $g=0.75$; if $2 < d/d_{0.05} < 4$ then $g=0.5$; if $d/d_{0.05} > 4$ then $g=0.25$.

- d is the “top particle size”, defined as the square-mesh screen that retains 5% of the material (dimension of length expressed in cm).
- β is a “liberation factor” (dimensionless) describing the degree of liberation of the critical component from the matrix. Totally liberated particles means $\beta=1$ and totally incorporated particles means $\beta=0$. Otherwise β can be calculated from:

$$\beta = \sqrt{\frac{L}{d}}$$

where: L is the liberation size

The FSE estimate is better to the extent that these parameters can be determined more precisely. However, this is not always easily possible in practice (without extreme expenditure of resources), whence some default parameter values may be used.

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Sampling of heterogeneous bottom ash from municipal waste-incineration plants

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Abstract

Bottom ash from waste-incineration plants is a very heterogeneous material and sampling requires special attention. The objective of the sampling should be carefully defined before a sampling protocol can be made. In Denmark, 500,000 tonnes of bottom ash is produced annually from a number of municipal and privately owned incineration plants. For legal reasons, the bottom ash has to be sampled and evaluated since reuse options of the bottom ash depends on comparing fixed thresholds with these analytical results. Legally, a sample of 5 kg has to be taken from every batch of 5000 tonnes of bottom ash. The amount of trace elements leaking into the environment (leachates) play the key role in deciding if and where bottom ash can be reused. Test for systematic error (bias) and estimation of the sampling and preparation errors were the main objectives of this study.

Three alternative methods of sampling, comprising mechanical sampling, “stopped belt sampling” and manual sampling from a stockpile have been evaluated and compared here. The primary and secondary sampling uncertainty is shown to be the dominant factor in the overall uncertainty of the analytical results. Stopped belt sampling of four different types of bottom ashes has been carried out in a baseline study to estimate the primary increment variance, enabling estimation of the different uncertainties associated with the final analytical result.

Based on this study, the owners and operators of incinerating plants in Denmark now recommend to the Danish Environmental Agency to revise the current governmental protocol for sampling of bottom ash in order to minimize the risk for biased samples and to significantly reduce the uncertainty of the final result.

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Keywords: Municipal waste; Bottom ash; Sampling

1. Introduction

Waste management has had top priority in Denmark during the last 20 years. The Danish Environmental Agency has encouraged development of programmes for reuse and recycling of a variety of different types of waste materials. As part of this programme, all non-reusable waste streams containing organic materials have to be stabilised by incineration before they are finally disposed of. Thus more than 2 million tonnes of municipal waste were incinerated in 2002 producing 500,000 tonnes of bottom ash.

Normally, raw bottom ash is stored 3 to 4 months before a sample is taken and analysed. During this period the bottom ash undergoes several chemical reactions, which stabilise the material and especially reduce the amount of

leachable trace metals. The analysis comprises a number of selected elements, Total Organic Carbon (TOC) and a leaching test to evaluate the amount of trace elements and salts that might leak from the bottom ash into the environment. The outcome of this test determines to which of four different categories the bottom ash belongs and hence where the bottom ash can be reused.

The Danish Environmental Agency has issued a sampling protocol [1] to be used for this characterisation of bottom ash from incineration of municipal waste. The accuracy and precision of the sample taken according to this sampling protocol has recently been questioned however. The owners and operators of waste-incineration plants in Denmark, organised in a network named DAFONET, have carried out a study of the fundamental sampling characteristics of bottom ashes from incineration plants and evaluated the accuracy of the existing official sampling protocol.

This study shows that the bottom ash is a very heterogeneous material indeed and that the current sampling

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protocol, which stipulates manual sampling, is prone to give significantly biased results. A proposal for an improved sampling protocol is presented.

2. Fundamental sampling characteristics of bottom ash from waste-incineration plants

The primary type of waste supplied to the municipal incineration plants is household waste. Various types of industrial waste streams are also incinerated, but the amount and type of this waste depends on the industry in the surrounding area. Thus, the feed stream to the incineration plants varies very considerably in time and from plant to plant.

Sampling of bottom ash from such waste-incineration plants consists of taking a number of increments forming a gross sample. Analysis is preceded by crushing and dividing the gross sample.

One of the important objectives of this study was to establish quantitative measures for the primary increment variance and to examine correlations between increments using the variogram technique. Bottom ash from four different incineration plants was tested in this study. All plants use moving grate furnaces with a wet bottom ash system.

The raw bottom ash was matured for 3 to 4 months before the test was carried out. During this time the raw bottom ash undergoes a number of chemical reactions including a carbonisation process. Generally, the leaching



Fig. 1. “Stopped belt sampling” of bottom ash from the conveyor belt. Absolute all particulate matter in the frame is excavated, including all fines.

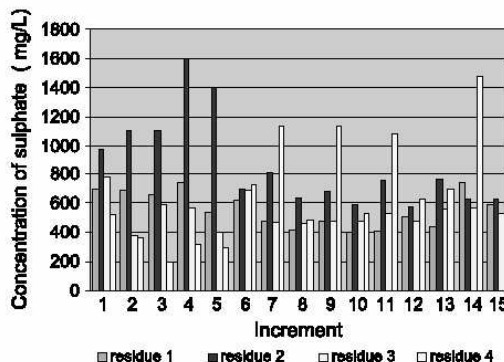


Fig. 2. Concentrations of sulphate in the eluate in the individual increments.

property of the bottom ash is reduced considerably during this maturing process.

The raw, matured bottom ash consists of a granular inorganic matrix, fragments of paper and smaller or larger pieces of iron and aluminium. Before any sampling is done, paper and metal impurities are removed in a screening drum, which also removes oversized (inorganic) particles. After this pre-treatment the bottom ash has a nominal top size of 40 mm.

The primary increments were collected from a conveyor belt, which was stopped regularly (“stopped belt sampling”) using a special sampling frame, see Fig. 1. A full cut of the bottom ash on the belt conveyor was sampled. The distance between the two sides of the sampling frame was five times the nominal top size of the bottom ash, and each primary increment weighed 7–10 kg. This method for collecting the primary samples ensured a representative, unbiased sample as all parts of the lot had an equal chance of being selected.

Each primary increment was crushed to 10 mm, riffled to 5 kg and finally crushed to 4 mm in a jaw crusher. The further sample preparation to an analysis sample followed the standardized procedure in Ref. [2].

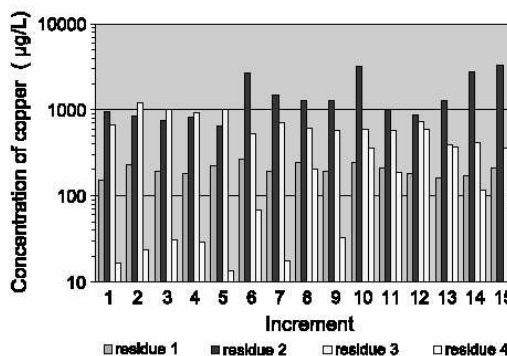


Fig. 3. Concentrations of copper in the eluate in the individual increments.

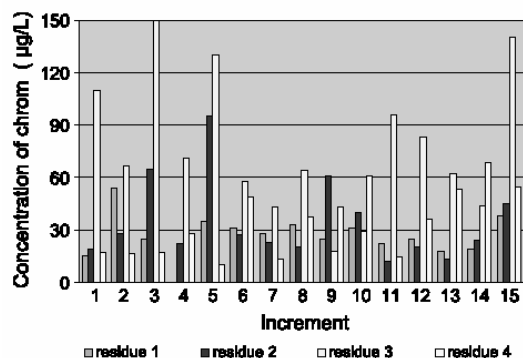


Fig. 4. Concentrations of chromium in the eluate in the individual increments.

In this study, 15 primary increments were each taken from the four different bottom ashes. A full characterization of bottom ash comprises determination of the total content of different trace metals as well as measurement of trace metals and salt concentration after a leach test [2]. In the present study, only leachable sulphate, copper and chromium were measured as these parameters normally determine which category the bottom ash belongs to.

The four different bottom ashes are labelled residue 1 to 4. The eluate concentration of sulphate (mg/l), copper and chromium (µg/l) in the individual increments are shown in Figs. 2–4.

Notice the logarithmic scale of the axis of ordinates in Fig. 3 indicating very substantial variations in the eluate concentration in the different increments. The level of concentration of the three measurants in the four different bottom ashes also varies considerably. Bottom ash 2 has the highest average eluate concentration of sulphate and copper.

Estimation of the primary increment variance is important when calculating the overall precision of the final result. For the conveyor belt sampling, the variogram-technique is used to evaluate serial correlation between increments (auto-correlation). The variogram is a plot of the variance as

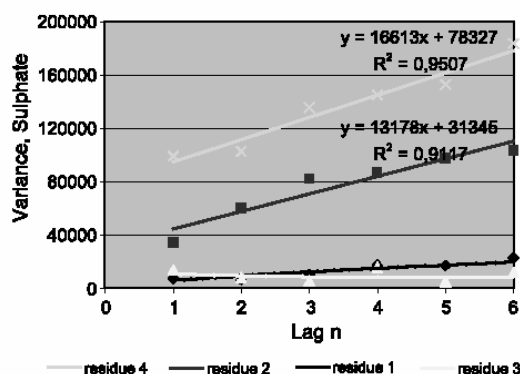


Fig. 5. Variogram for sulphate.

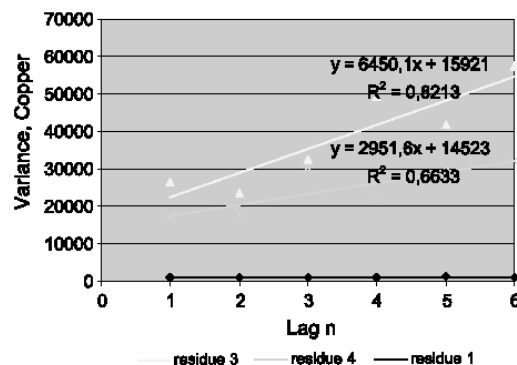


Fig. 6. Variogram for copper (medium levels leachable copper: 50–1000 µg/l).

function of the interval, called lag, between increments. The value of the variance $V(k)$ at lag n is calculated by the expression [3]:

$$V(k) = \frac{\sum_{i=1}^{i=N_k} (x_{i+k} - x_i)^2}{2N_n}$$

where x_{i+k} and x_i are the measured values for increment $i+k$ and i , respectively, while N_n is the number of pairs of increments at lag k apart. The variograms up till lag 6 for sulphate, copper and chromium in the four bottom ashes are shown in Figs. 5–8, where lag k is measured in time, i.e. 1 lag = 15 min.

For sulphate the increments seem to be auto-correlated in bottom ashes 2 and 4, whereas the increments in bottom ashes 1 and 3 are clearly without serial correlation. For copper and chromium similar differences are seen. The eluate concentration of copper normally determines the category of the bottom ash, and in Figs. 6 and 7, it appears that leachable copper in bottom ash is not correlated—at least when the increments are separated by more than 4 to 6 lags, i.e. 60 to 90 min. Consequently, in the following sections of this study, increments will be assumed to be independent. This simplification has the consequence that

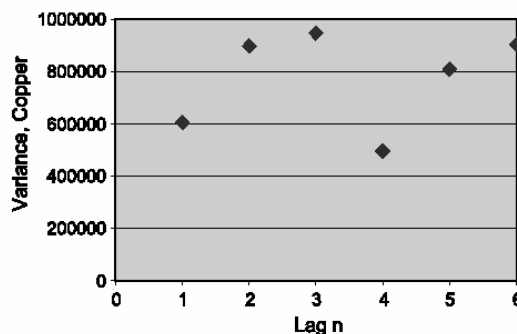


Fig. 7. Variogram for copper (high levels leachable copper: 1000–3300 µg/l).

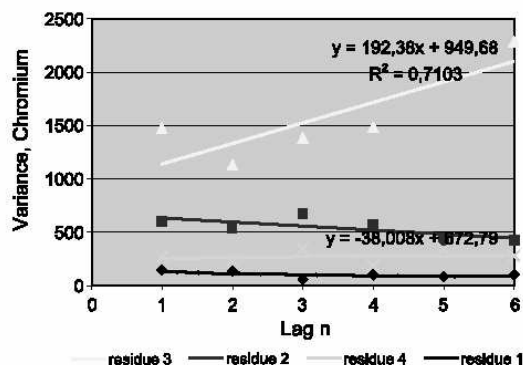


Fig. 8. Variogram for chromium.

the calculated sampling uncertainty might be too conservative, i.e. too high, which is considered a reasonable safety guard.

3. Comparison of different sampling schemes

The current sampling protocol to be used in Denmark for sampling of solid bottom ash from incineration plants [1] comprises the following steps:

- Fifty increments of approx. 2 kg each are sampled manually, either from freshly produced bottom ash from the incinerating plant or from a stockpile to form a gross sample. The increments should be distributed evenly over the entire lot size of 5000 tonnes.
- The gross sample is sieved in a 45-mm sieve. Oversize particles are crushed and added to the gross sample, whereas materials as metals, glass and paper are removed.
- The sample mass is reduced to 5 kg by riffing the gross sample, followed by a new size reduction to 4 mm using a jaw crusher.
- In a riffle divider, the 5 kg sample is split into two halves of which one is used in the leaching test according to Ref. [2].

In this study, the accuracy and precision of this sampling protocol is examined by comparing it with two alternative sampling schemes, namely mechanical sampling from a falling stream and “stopped belt sampling” from a conveyor belt. The latter is generally accepted as the reference method when comparing different sampling methods [3]. Test for systematic error (bias) and estimation of the sample preparation error were the main objectives of this study.

Iron, paper and other non-breakable impurities must be removed from the bottom ash before mechanical sampling is possible, otherwise these impurities will clog the primary cutter. In this trial, the bottom ash was screened in a

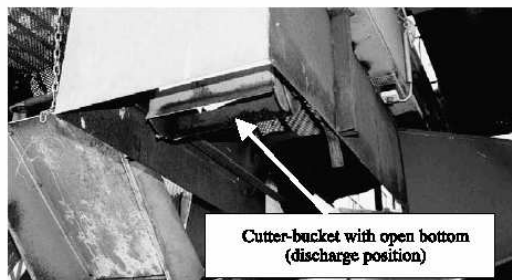


Fig. 9. Mechanical cutter-bucket for sampling increments from a free-falling stream of bottom ash.

screening drum before sampling. The nominal top size of the bottom ash after screening was 40 mm and the capacity of the conveyor belt was 100–200 tonnes/h.

The mechanical sampler used was a cutter-bucket type, see Fig. 9. The width of the bucket was 200 mm, i.e. five times the nominal top size of the screened bottom ash. The linear velocity of the bucket was 0.6 m/s, which is generally accepted [3,4] as the upper limit for a bucket type of sampler to avoid a biased increment. The sample was taken from a free-falling stream.

The manual samples were taken directly from the surface of the stockpile, see Fig. 10. Three sets of manual samples, labelled A, B and C were taken to evaluate the reproducibility (precision) of this method (also known as grab sampling).

3.1. Comparison of three alternative sampling methods

Twenty sets of samples (each set comprising three manual sampled increments, one increment sampled with the mechanical bucket and one “stopped belt sample”) were taken at approx. 15-min intervals. The mechanical and the “stopped belt” samples were typically 10 kg each, whereas the manual samples were 2 kg each. The mechanically sampled incre-



Fig. 10. Manual sampling (grab sampling) of bottom ash from a stockpile. This is the officially recommended procedure.

ments and the “stopped belt samples” were crushed to 10 mm nominal top size before any further mass reduction was made. The mechanically sampled increments were pooled and divided in a rotating tube divider, while the “stopped belt samples” were reduced to 5 kg using a riffle divider. The sample preparation and analysis variances were estimated by analysing the 20 “stopped belt samples” in duplicate.

The “stopped belt samples” are unbiased, representative samples of the true (unknown) composition [3] of the bottom ash. Thus, the grand means of these 20 analytical results are the best baseline estimators of the true values of these analytes, and using the standard deviation of the results, appropriate 95% confidence intervals can be calculated.

The results of the three different sampling methods are summarized and compared in Table 1. The mechanical sample is a composite sample consisting of 20 increments. The three manual samples are also composite samples each consisting of 20 increments. The results under the heading “Stopped belt sampling” are the average values of 20 “stopped belt samples”, which have been prepared and analysed individually. Thus, a 95% confidence interval can be assigned to the values listed as “stopped belt sampling”.

3.2. Comparison—discussion

The confidence interval for sulphate is relatively wide so all three results of the manual sampling fall inside the confidence interval although samples A and C are near the lower limit of the confidence interval.

Leachable copper in the 20 “stopped belt samples” varied from 15 to 600 µg/l and hence it was not possible to get a reliable reference value for copper. Variations in pH and organic materials in the individual stopped belt samples are believed to have caused this considerable variation in copper. On the other hand, the mechanical sample and the manual samples are in good agreement. The results for chromium on the other hand clearly indicate that the manual samples are biased, whereas the mechanical sample is identical with the reference value.

For conductivity (sample A and C) and moisture (A, B and C) the manual samples are all biased with low values. Again, the mechanical sample shows satisfactory results compared with the reference values.

Table 1
Sampling of bottom ash using three different sampling methods

Parameters	Mechanical sampling	Manual sampling			“Stopped belt sampling”
		A	B	C	
Sulphate, mg/l	855	774	857	745	916 ± 223
Copper, µg/l	50.2	45.4	44.9	55.1	—
Chromium, µg/l	30.0	54.3	63.0	13.3	30.8 ± 8
Conductivity, mS/cm	6.04	5.25	5.70	5.29	6.0 ± 0.56
pH	10.15	10.05	9.94	10	9.98 ± 0.31
Moisture, %	15.1	12.5	13.5	12.4	15.2 ± 1.5

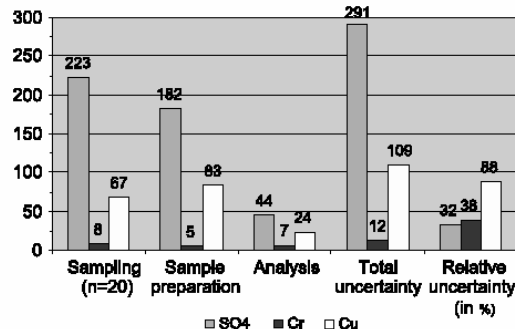


Fig. 11. Decomposition of sampling uncertainties, sample preparation and analysis of bottom ash with no crushing before mass reduction.

Manual sampling is prone to give biased results if the analyte varies with the particle size. Generally, for coarse particle materials, manual samples will not have the same particle size distribution as the lot, and this may result in a biased sample. In order to evaluate the concentration of chromium three size fractions (<4 mm, 4–16 mm and >16 mm) has been measured. The concentration in the fine fraction (<4 mm) is 10 times higher than in the intermediate size fraction (4–16 mm). As the manual samples are taken from a stockpile and each increment is only 2 kg each, this variation of chromium as function of particle size is most likely the explanation for the bias of the manual sampling.

4. Estimation of the uncertainties of sampling, sample preparation and analysis

The variance of sample preparation and analysis has been estimated by duplicate analysis. In part 2, the variance of sampling was examined in some detail and it is concluded that for the scale used to sample bottom ash from municipal

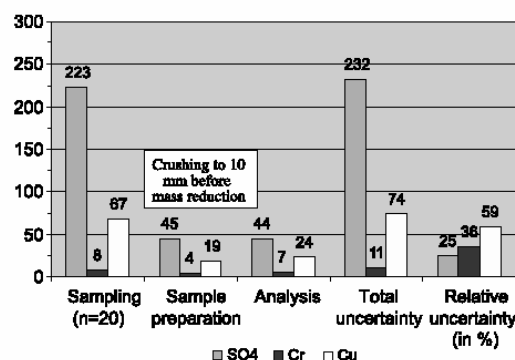


Fig. 12. Decomposition of sampling uncertainties, sample preparation and analysis of bottom ash with crushing to 10 mm before mass reduction.

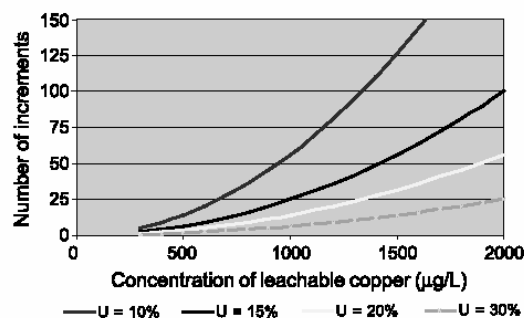


Fig. 13. Uncertainty of the final analytical result as a function of number of increments.

waste-incineration plants, no significant serial correlation between the increments can be observed.

The resulting uncertainty, U , expressed as two times the standard deviation, is in this case given by:

$$U = \pm 2 \cdot \sqrt{\left(\frac{V_1}{n}\right) + V_{PT}}$$

where V_1 is the primary increment variance, V_{PT} is the variance of sample preparation and testing (analysis), while n is the number of increments in the gross sample.

The uncertainties of sampling, sample preparation and analysis for a sampling scheme, where a mechanical cutter is used to collect 20 increments to form a gross sample, are shown in Figs. 11 and 12. In Fig. 11, the sample preparation comprises division of the gross sample to 5 kg without crushing before division, i.e. following the sample preparation procedure laid down by the Danish Environmental Agency [1]. In Fig. 12, the gross sample is crushed to 10 mm nominal top size before division, which results in a significant reduction of the uncertainty associated with sample preparation.

4.1. Error decomposition—discussion

For sulphate and copper, the sampling error is the dominant factor to the overall uncertainty. Increasing the number of increments in the gross sample is the most effective step to reduce the uncertainty of the final result.

The concentration of leachable copper normally determines which of the four categories a specific bottom ash belongs to. The majority of bottom ashes are category-3 with copper varying from 1000 to 2000 µg/l. At this relatively high level of copper, the variance of sample preparation and testing, V_{PT} , is insignificant compared to the sampling variance. Hence the overall uncertainty, U , can be simplified to:

$$U \approx \pm 2 \cdot \sqrt{\left(\frac{V_1}{n}\right)}$$

The uncertainty (as percentage of the measured value of leachable copper) as function of number of increments in the gross sample is shown in Fig. 13. To obtain an uncertainty of 15% equivalent to ± 300 µg/l at 2000 µg/l, 100 increments are needed.

Fig. 13 indicates that bottom ashes with a level of leachable copper of approx. 2000 µg/l cannot be measured with uncertainty lower than 15%. A lower uncertainty would require an unrealistically high number of increments to be sampled.

5. Conclusions

Bottom ash from waste-incineration plants is a very heterogeneous material and sampling and analysis requires special attention and the utmost care in planning. The objective of the sampling should be carefully defined before a sampling protocol can be made.

In Denmark, 500,000 tonnes of bottom ash is produced annually from a number of municipal and privately owned incineration plants. For legal reasons, the bottom ash has to be sampled and evaluated as the reuse of the bottom ash depends on the results of the analysis. Therefore, the sampling protocol must minimise the risk of taking a biased sample and the overall reproducibility (precision) should be sufficient to enable the producer to establish—with a high degree of confidence—to which category the bottom ash belongs.

This study has demonstrated that mechanical sampling from a falling stream of bottom ash is the preferred sampling method. Manual sampling must be completely avoided, as it will invariably result in significantly biased samples. Mechanical sampling makes it immensely much more easy to take an appropriate number of increments, whereby the uncertainty associated with sampling can be reduced to an acceptable level.

The nominal top particle size, and the mass of the final samples, have to be taken into consideration when the procedure for sample preparation is designed. A significant reduction of the sample preparation error was obtained in this study simply by crushing the original increments to 10 mm top size before the mass reduction was carried out.

References

- [1] Energi-og Miljøstyrelsens bekendtgørelse nr 655, "Bekendtgørelse om genanvendelse af restprodukter og jord til bygge-og anlægsarbejder, 27. juni 2000 (Danish Environmental Agency, Departmental Order no. 655 "Departmental Order on how to reuse residues and bottom ash from waste incinerating plants as materials for constructions work", June 2000).
- [2] CEN prEN 12457-3, "Characterisation of waste—Leaching—Compliance test for leaching of granular waste materials and sludge—Part 3".
- [3] International Standard, ISO 13909, Hard coal and coke—Mechanical sampling, Part 1-8.
- [4] P. Gy, Sampling of Heterogeneous and Dynamic Material System, Elsevier, 1992.



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- Variances
- Statistics on counting
- Errors in sampling

- The fundamental sampling error
- The minimum practical error

1

Variances



Pierre Gy 1998:

- That everyone becomes aware of the **additivity** of errors, of biases, and **of the variances of sampling and analysis**

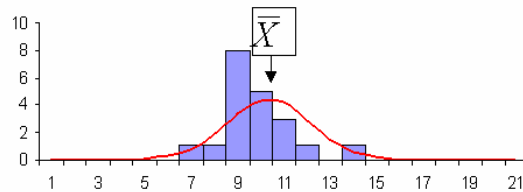
- Variances are additive!
- Standard deviation = $\sqrt{\text{Variance}_1 + \text{Variance}_2 + \dots}$

2



The standard deviation is a measure of the spread of the values

$$s = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$



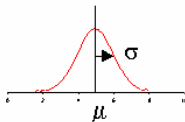
68 % of the values are within: $\bar{X} \pm s$

95 % of the values are within: $\bar{X} \pm 1.96s$

3



Normal distribution ?



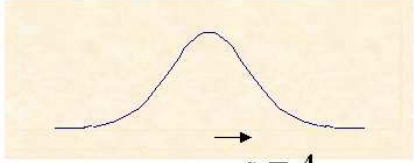
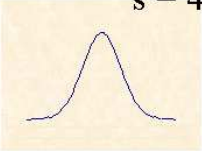
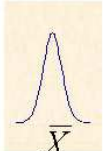
- Do the values follow a normal distribution?
- In many/most cases - NO!
- Can we then use this kind of statistics?
- YES - because the mean of the values \bar{X} will follow a normal distribution, provided that the number of measurements are 'high enough'

'The CENTRAL LIMIT THEOREM'

4

Standard deviation and variance



	Stdev. s	Variance s^2
	4	16
	2	4
	1	1
mg/l	mg/l	(mg/l) ²



Uncertainty propagation law

For a function:

$$x = f(p, q, r, \dots)$$

holds:

$$s_x^2 = \left(\frac{\partial x}{\partial p} \right)^2 s_p^2 + \left(\frac{\partial x}{\partial q} \right)^2 s_q^2 + \left(\frac{\partial x}{\partial r} \right)^2 s_r^2 + \dots$$

provided that all the variables are stochastic and independent



Addition and subtraction:

$$y = kx + w - z$$

VARIANCES ARE ADDITIVE:

$$s_y^2 = k^2 s_x^2 + s_w^2 + s_z^2$$

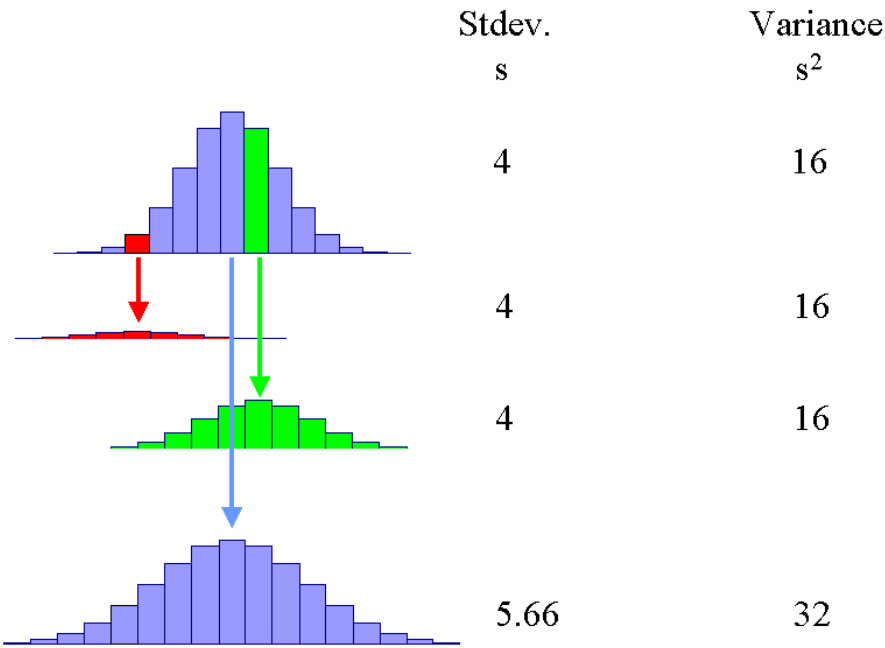
Multiplikation and division:

$$y = \frac{kx \cdot w}{z}$$

RELATIVE VARIANCES ARE ADDITIVE:

$$\frac{s_y^2}{y^2} = \frac{s_x^2}{x^2} + \frac{s_w^2}{w^2} + \frac{s_z^2}{z^2}$$

7



8

When is a variation insignificant?



$$s_{Total} = \sqrt{s_{Sampling}^2 + s_{Analysis}^2}$$

$$s_{Sampling} = 10$$

$$s_{Analysis} = 10, 5, 3, 2, 1 \text{ ???}$$

Standard deviations	
$s_{Analysis}$	s_{Total}

10	14.1
5	12.2
3	10.4
2	10.2
1	10.1

Variances	
$s_{Analysis}^2$	s_{Total}^2

10	200
5	125
3	109
2	104
1	101

9

How big is the standard deviation of the standard deviation?



How many measurements/samples should be used, in order for the standard deviation to be within 18 % of the correct value in 95 % of the experiments ??

95 % tolerance interval for the standard deviation:

n	Upper limit %	Lower limit %
10	56	62
100	18	18
1000	6	6

10



What is the standard deviation of counting 100 random events?

If it follows a Poisson distribution, then:

Mean = n

Variance = n

Standard deviation = $\sqrt{n} = 10$

n	s	$RSD \%$
10	3	31.6
100	10	10.0
1000	32	3.2
10000	100	1.0
100000	316	0.3
1000000	1000	0.1

11



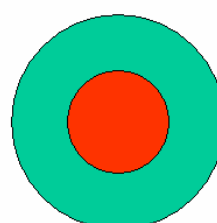
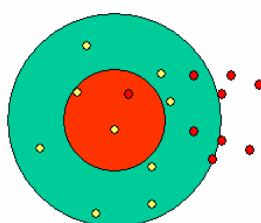
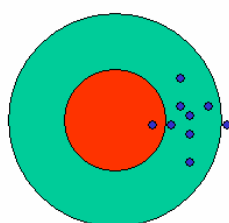
12



Systematic error

Random
uncertainty

Gross error



13



Systematic error

TRUENESS

$$Bias = \delta = \bar{X} - \mu$$

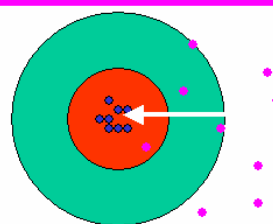
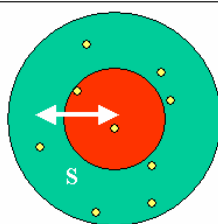
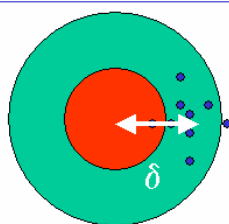
Random
uncertainty
PRECISION

$$s = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$

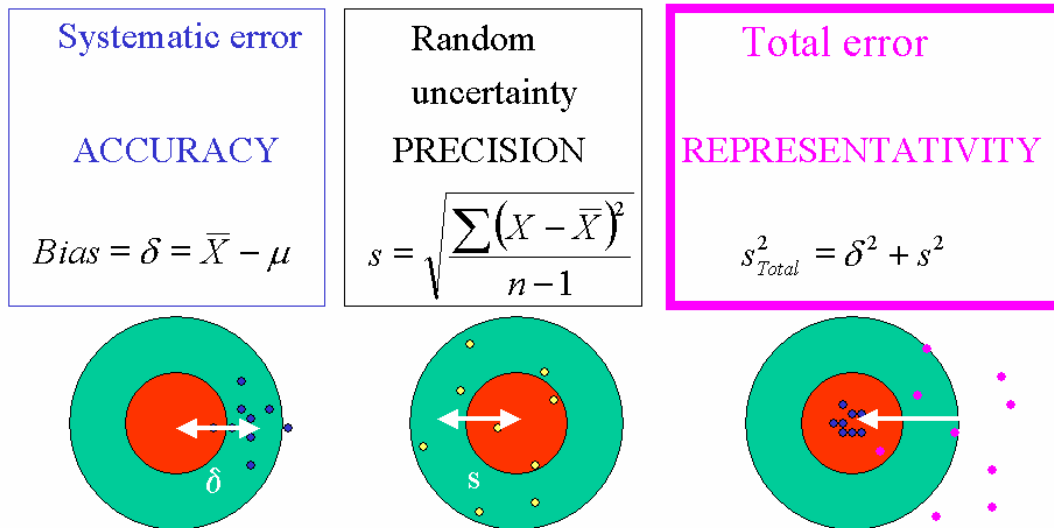
Total error

ACCURACY

$$s_{Total}^2 = \delta^2 + s^2$$



14

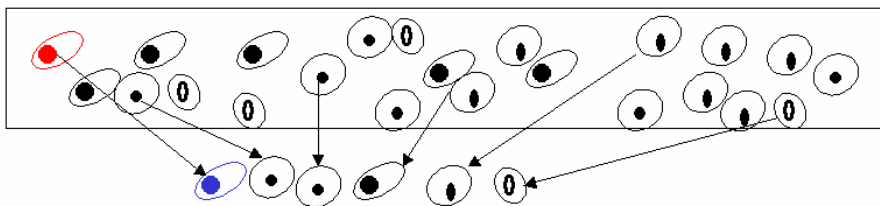


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The Fundamental Sampling Error (FSE)



Definition: "The sampling error that occurs when the increment selection is **correct**, and when the **increments** making up one sample contains one single **fragment**"



FSE is only caused by the constitutional heterogeneity CH_L

$$m(FSE) \cong 0 \qquad s^2(FSE) = \frac{1-P}{PN_F} CH_L$$

P : Selecting probability

N_F : number of fragments in lot

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Heterogeneity Invariant (HI_L)



Using $P = \frac{M_S}{M_L}$

$$s^2(FSE) = \frac{1-P}{PN_F} CH_L = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) \cdot CH_L \cdot \frac{M_L}{N_F}$$

Defining: $HI_L = CH_L \cdot M_F$ we get finally:

$$s^2(FSE) = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) \cdot HI_L$$

*HI_L can be estimated from
 $s^2(FSE)$ – and vice versa*

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HI_L and Gy's formula (for $M_S < M_L$)



$$s^2(FSE) \cong \frac{HI_L}{M_S} \approx \frac{c\beta fgd^3}{M_S}$$

HI_L is the sample mass in g that gives a sampling standard deviation of 100 %

The usual sampling constant K used in analytical chemistry (Ingamells and Switzer 1973):

K is the sample mass in g that gives a sampling standard deviation of 1 % i.e.:

$$K = 10^4 HI_L$$

18

Approximation of HI_L from Gy's formula:



$$HI_L = c\beta fgd^3$$

c: constitutional factor
f: particle shape factor
g: size distribution factor
 β : liberation factor
d: top particle size

Derived for mineralogical samples, and works best for binary mixtures of particulate material, where the critical component is present in separate fragments

Derivation of Gy's formula
see next pages

19

$$HI_L = \sum_i \frac{(a_i - a_L)^2}{a_L^2} \cdot \frac{M_i^2}{M_L}$$



Using 3 approximations we get:

$$HI_L = \left(\sum_j v_j \frac{M_{Lj}}{M_L} \right) \left(\sum_k \rho_k \frac{(a_k - a_L)^2}{a_L^2} \cdot \frac{M_{Lk}}{M_L} \right)$$

Size classes

Density classes

$$IH_L = (fgd^3) \cdot (c\beta)$$

Volume of cc-containing fragment

Density-concentration function of cc-containing fragment²⁰



Size class parameters:

$$fgd^3 = \left(\sum_j v_j \frac{M_{Lj}}{M_L} \right)$$

d : The top size of particles

f : The shape factor so that: $v_{jk} = f_j d_j^3$

g : The granulometric factor: g = ratio between volume of the top size fragments and average cc-containing fragments (?)

fgd^3 = Volume of cc-containing fragments, V_{cc}

21



Density class parameters:

$$c\beta = \left(\sum_k \rho_k \frac{(a_k - a_L)^2}{a_L^2} \cdot \frac{M_{Lk}}{M_L} \right)$$

For a "worst case" with only 2 kind of fragments:

M: Pure critical component, $a_L = 1, \rho_{cc}$

g: Pure matrix (gangue), $a_L = 0, \rho_g$

β : Total liberated = 1

Thus $M_{LM}/M_L = a_L$ and $M_{Lg}/M_L = (1-a_L)$ and:

$$c\beta = \frac{(1-a_L)}{a_L} \cdot [(1-a_L) \cdot \rho_{cc} + a_L \cdot \rho_g]$$

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For low concentrations, $a_L < 0.1$

$$c\beta = \frac{(1-a_L)}{a_L} \cdot [(1-a_L) \cdot \rho_M + a_L \cdot \rho_g] \cong \frac{(1-a_L)}{a_L} \cdot \rho_{cc}$$

$$fgd^3 = V_{cc}$$

$$V_{cc} \cdot \rho_M = M_{cc}$$

$$HI_L \cong \left(\frac{1}{a_L} - 1 \right) \cdot M_{cc}$$

M_{cc} : Mass of one critical component containing fragment

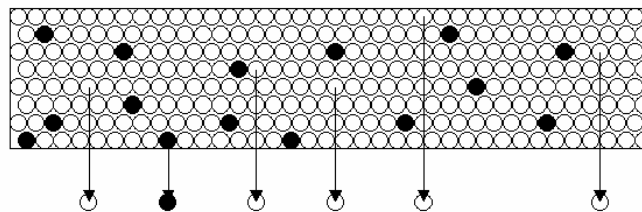
When the concentration in the fragments is α instead of 1:

$$HI_L \cong \left(\frac{\alpha}{a_L} - 1 \right) \cdot M_{cc}$$

23



Classical statistics



Selecting fragments one-by-one

The binomial distribution gives:

$$\mu = n \cdot p = \frac{M_S}{M_{cc}} \cdot a_L \quad \sigma^2 = n \cdot p \cdot (1-p) = \frac{M_S}{M_{cc}} \cdot a_L \cdot (1-a_L)$$

$$s^2(FSE) = \frac{\sigma^2}{\mu^2} = \left(\frac{1-a_L}{a_L} \right) \cdot \frac{M_{cc}}{M_S} = \frac{HI_L}{M_S} \Rightarrow HI_L = \left(\frac{1}{a_L} - 1 \right) \cdot M_{cc}$$

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For trace concentrations



$$HI_L = \left(\frac{1}{a_L} - 1 \right) \cdot M_{cc} \xrightarrow{a_L < 0.1} HI_L = \frac{M_{cc}}{a_L}$$

The heterogeneity invariant HI_L is simply the amount of material in g, that contains 1 – one – fragment of the critical compound !

The distribution is thus poisson and not binomial i.e.:

$M_S = n \cdot HI_L = n_{cc}$	$\sqrt{n_{cc}}$	$s^2(FSE) \%$
1	1	100
100	0.1	10
10,000	0.01	1
1,000,000	0.001	0.1

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Example: Sampling 1 ppm Au



Sampling parameters			M_s, g at RSD%		
$r, \mu m$	M_{cc}, g	HI_L, g	100%	10%	1%
100	8,08E-05	81	81	8084	808436
10	8,08E-08	8,1E-02	8,1E-02	8	808
1	8,08E-11	8,1E-05	8,1E-05	0,008	0,808
atom	3,27E-22	3,3E-16	3,3E-16	3,3E-14	3,3E-12

$$HI_L = \frac{M_{cc}}{a_L}$$

$$s^2(FSE) = \frac{HI_L}{M_S}$$

$$M_S = \left(\frac{HI_L}{RSD\% / 100\%} \right)^2$$

26

Example: Sampling 1 ppm Au



Sampling parameters			RSD% at M_s, g		
$r, \mu m$	M_{cc}, g	HI_L, g	0,5	2	10
100	8,08E-05	81	1271,6	635,8	284,3
10	8,08E-08	8,1E-02	40,2	20,1	9,0
1	8,08E-11	8,1E-05	1,3	0,6	0,3
atom	3,27E-22	3,3E-16	2,6E-06	1,3E-06	5,7E-07

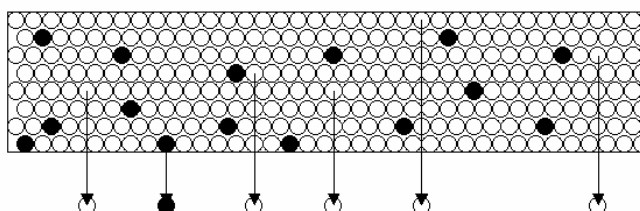
$$HI_L = \frac{M_{cc}}{a_L}$$

$$s^2(FSE) = \frac{HI_L}{M_s}$$

$$RSD\% = 100\% \sqrt{\frac{HI_L}{M_s}}$$

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Selecting fragments one-by-one



Correct
sampling:

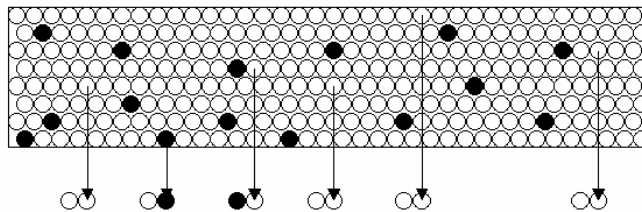
Each fragment must have the
same non-zero probability of
being taken into the sample

Grouping and
segregation error:

When fragments are
not sampled one-by-
one

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Selecting fragments in groups (increments)



Distributional heterogeneity:

$$DH_L = \frac{1+YZ}{1+Y} \cdot CH_L$$

Number of
fragments
in a group

Y: Group size parameter $\approx N_g$

Z: Segregation parameter

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Distributional heterogeneity



$$DH_L = \frac{1+YZ}{1+Y} \cdot CH_L$$

$$Y = \frac{N_F - N_G}{N_G - 1} \quad \text{For } N_G > 1 \quad Y \cong \frac{N_F}{N_G} - 1 = N_g - 1$$

$$DH_L \cong \frac{1+Z(N_g-1)}{N_g} \cdot CH_L \quad DH_L \approx \left(\frac{1}{N_g} + Z \right) \cdot CH_L$$

Smaller heterogeneity:
Average over N_g fragments

Greater heterogeneity:
Grouping and segregation

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Fundamental error

Minimum practical error

$$s^2(FSE) = \frac{1-P}{PN_F} CH_L$$

$$s^2(MPE) = \frac{1-P}{PN_G} DH_L$$



$$s^2(FSE) = \frac{HI_L}{M_S}$$

$$\xleftarrow{\begin{matrix} Z=0 \\ \text{or } N_g=1 \end{matrix}}$$

$$s^2(MPE) \cong \frac{HI_L}{M_S} \cdot (1 + Z(N_g - 1))$$

$$\downarrow Z=1$$

Remember: $\frac{N_F}{N_G} = N_g$

$$DH_L \approx \left(\frac{1}{N_g} + Z \right) \cdot CH_L$$

$$s^2(MPE) = \frac{HI_L}{M_S} \cdot N_g$$

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Minimum practical error

Comminution:
Reduce the SIZE of the
cc FRAGMENTS

**Incremental
Sampling:**
Take as MANY
INCREMENTS
as possible

$$s^2(MPE) \approx \frac{HI_L}{M_S} \cdot (1 + ZN_g)$$

Statistics:
Take as BIG a
SAMPLE as needed

Homogenize:
MIX, STIR
and BLEND

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Conclusion

- Variances are additive $s/3$ can be neglected
- Statistics on counting $s(n) = \sqrt{n}$
- Errors in sampling $Representativity = s^2 + \delta^2$
- The fundamental sampling error $s^2(FSE) \cong \frac{HI_L}{M_S} \approx \frac{c\beta f g d^3}{M_S}$
- The minimum practical error $s^2(MPE) \approx \frac{HI_L}{M_S} \cdot (1 + ZN_g)$
- Thank you for your attention bs @ kiku.dk 33

Sampling and Inventories at Thule Greenland. A case Study

Mats Eriksson

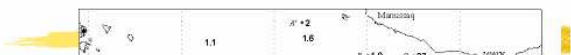


***“evaluation of small scale spatial variance in
the Pu sediment concentration”***

Problems

- Heterogeneous
- small sub samples (representative sampling)
- particles
- insufficient “up locking” of hot particles (HF-results)
- Measuring limitations

Marine Sampling

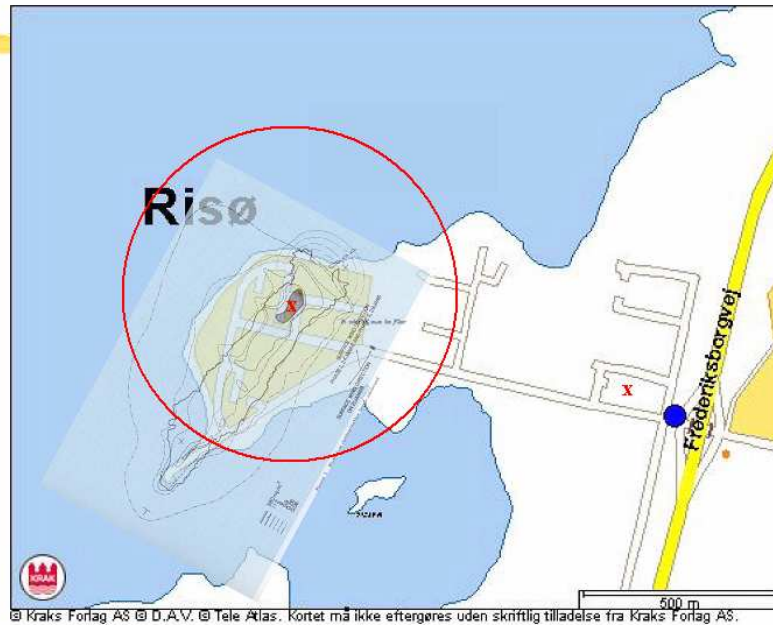


Gezinti sediment sampler



Geminisling

Unrepresentative, biased samples



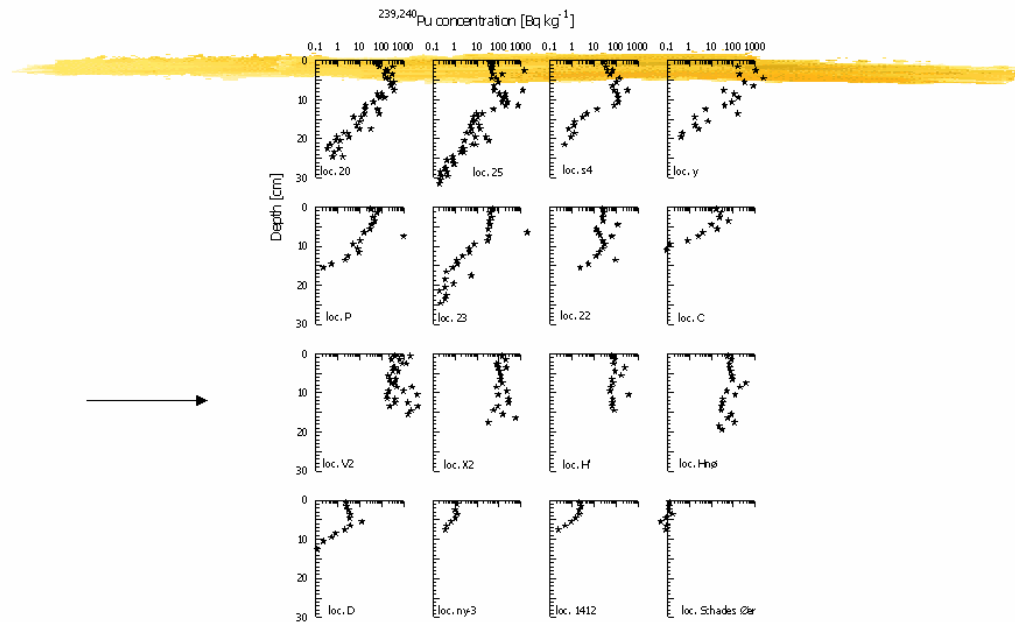
Sampling

HAPS

Gemini

Sediment sampling

Sampling limitations



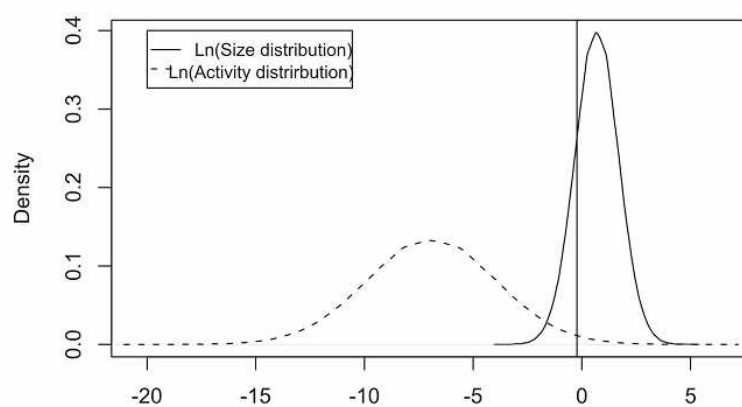
Gemini slice Wormhole, 15 cm sediment depth



HAPS sediment / gravel core, Thule-97, loc A

Particle distribution

Log-transformed particle size and activity distributions



Radiochemistry

Chemical from: PuO_2

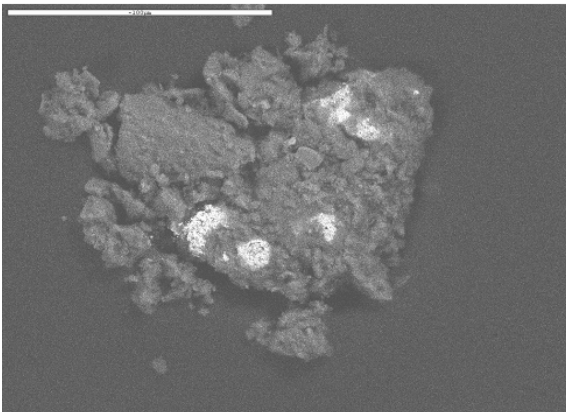
- PuO_2 is chemically highly inert

-”... it dissolves extremely slowly and incompletely in hydrochloric or nitric acids, except in the presence of small quantities of hydrofluoric acid.”

C. Keller (1971)

-Dissolution test on low level Pu samples from Thule Sediments. Up to 40 % remain undissolved in the samples when using the method described by Talvitie (1971)

HF-test

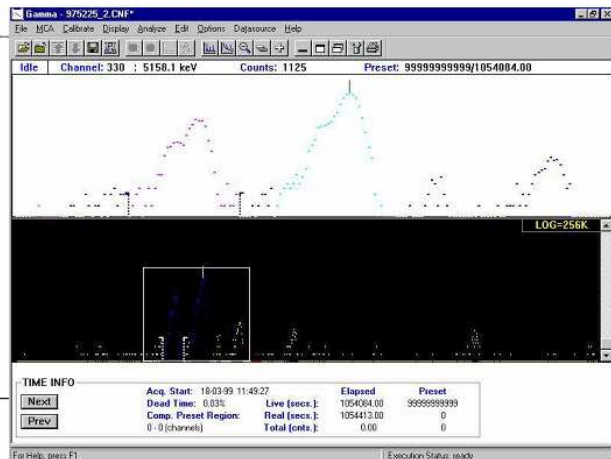
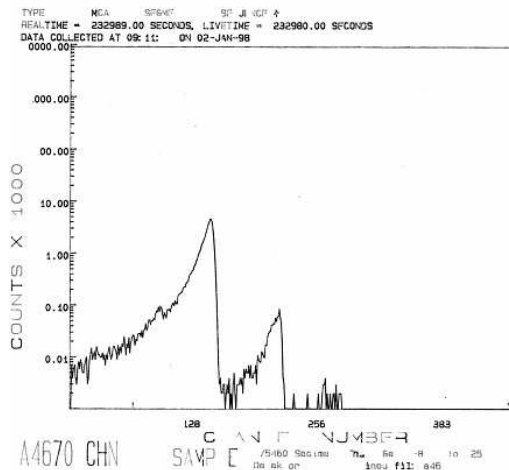


- Five samples tested
- missed Pu 9-31%
(*Aqua Regia*)

Alpha spectra

Low resolution spectra

High resolution spectra



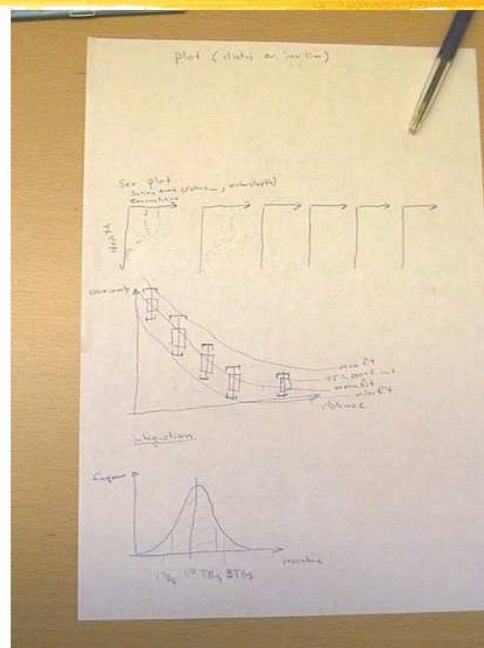
Design of the experiment

- Gamma screening measurement of the Pu-241 daughter, Am-241
- Counting time ~3000 s
- Simulation of the results

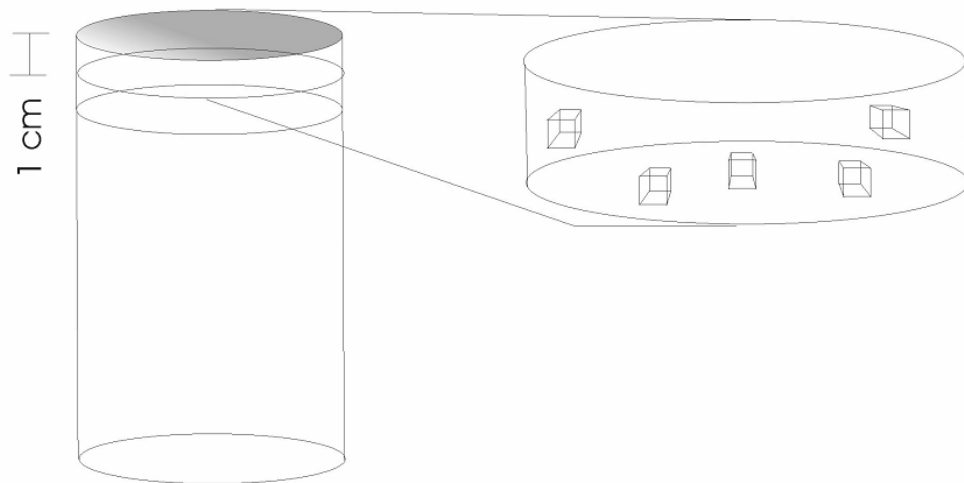
Screening experiment

- 5 sub-samples from each sediment slice
- sub-sample equal size as for alpha (i.e. 1 g)
- 6 locations
- In total 440 samples

Goals with the experiment



Sub-sampling from core



Core Combinations

section=1		Combinations = $5; 5^1$
section=2		Combinations = $5*5; 5^2$
section=3		Combinations = $5*5*5; 5^3$
⋮	⋮	⋮
section=N		Combinations = $5*...*5; 5^N$

Program

```

---

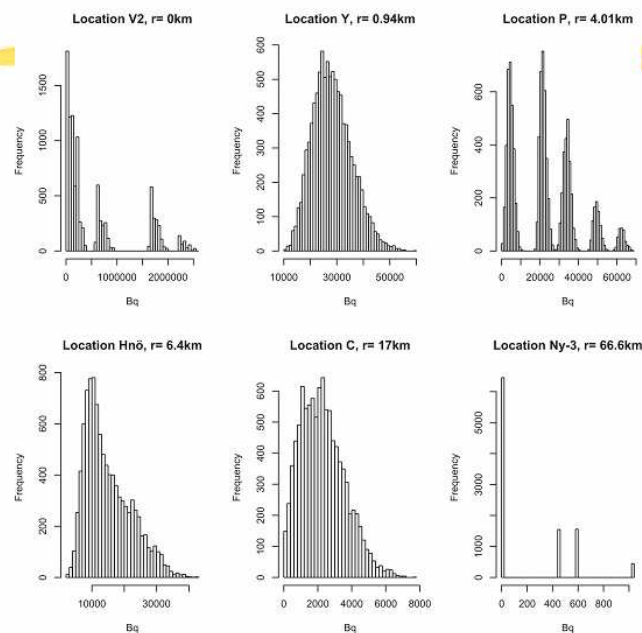
#location1
loc1<-c(1:10000)
for (ii in 1:10000){
a<-screening$"inv_i"[screening$distance==0.01]
b<-sample(5,length(a)/5,T) #random subsample
bb<-numeric(length(a))
for (i in 1:length(b)){bb[b[i]+((i-1)*5)]<-b[i]}
aa<-matrix(1:(2*length(a)), ncol=2)
aa[,1]<-screening$subsampling[screening$distance==0.01]
aa[,2]<-a
insum<-numeric(length(a))
insum<-a[aa[,1]==bb]
loc1[ii]<-sum(insum)}

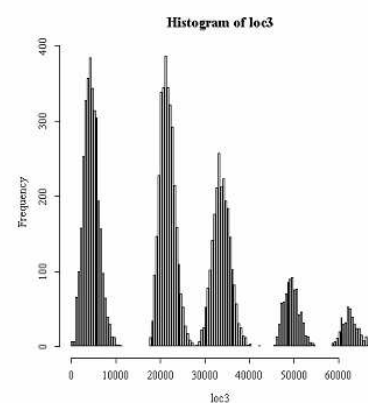
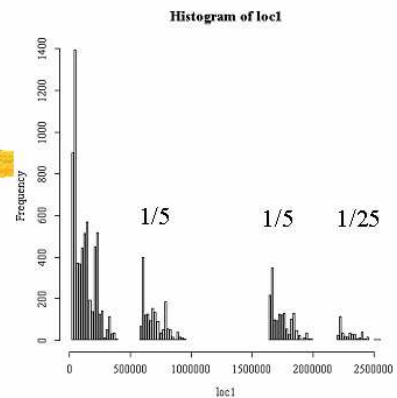
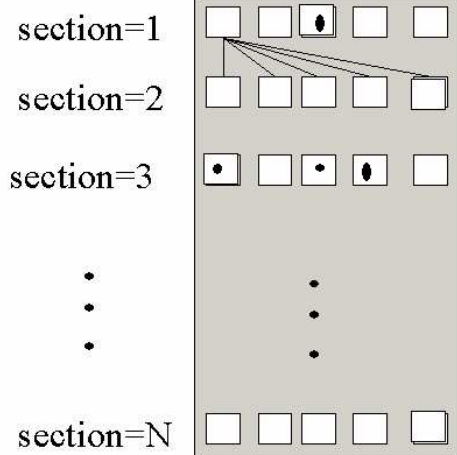
---

res<-c(summary(loc1),summary(loc2),summary(loc3),
summary(loc4),summary(loc5),summary(loc6))
ress<-matrix(res,nrow=6,ncol=6,T)
ress

```

Core inventory [Bq m⁻²]

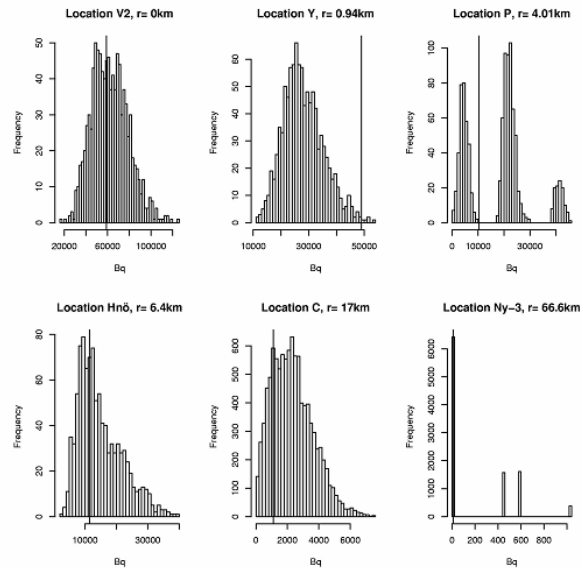




Site inventory

Loc	Min	1 Qu	Median	Mean	3 rd Qu	Max	Alpha
V2	15270	68930	212200	561100	722800	2561000	58938
Y	10090	22920	27640	28250	32980	59940	49072
P	356	5642	21820	23040	33860	68870	10321
Hnö	2247	9456	13120	14940	19520	42600	11548
C	0	1277	2167	2290	3110	7630	1138
Ny-3	0	0	0	206	446	1028	24

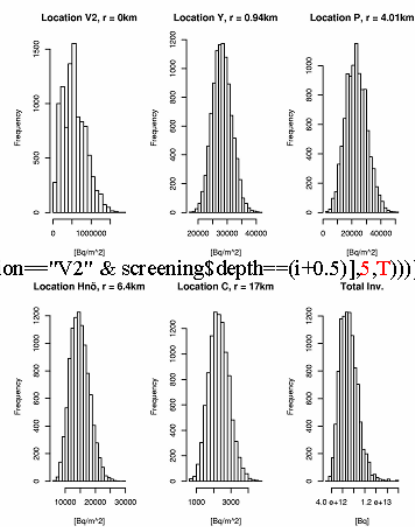
Check of the results



Bootstrap

```
sim<-10000
```

```
#location V2
ddaaV<-c(1:sim)
ddddd<-c(1:14)
for(ii in 0:sim){
  for(i in 0:13){
    ddddd[i+1]<-(mean(sample(screening$`inv.i`[screening$station=="V2" & screening$depth==(i+0.5)],5,T))))
    ddaaV[ii]<-sum(ddddd)}
  ...
}
```

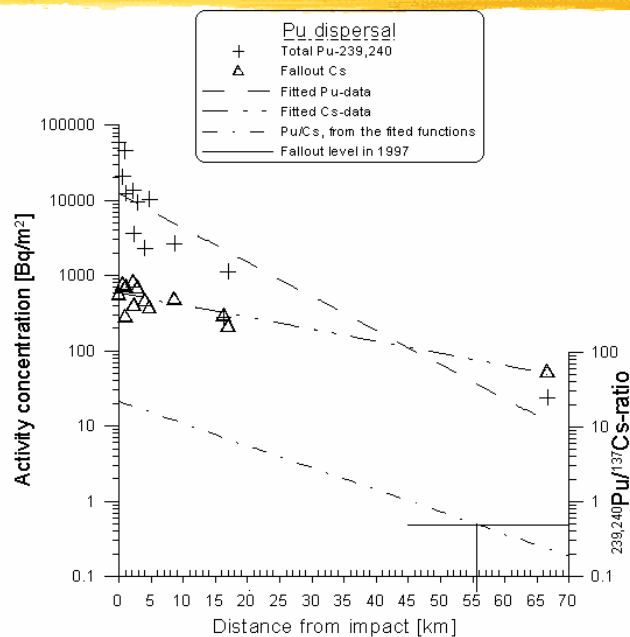


Integration

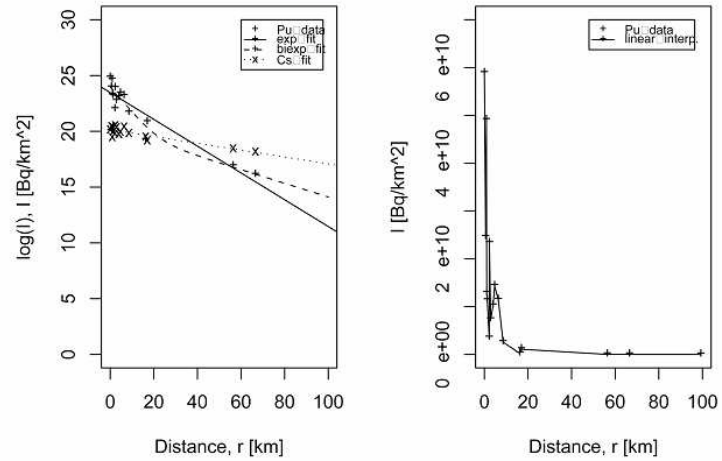
$$I = \iint_{\Omega} A(x, y) dx dy = \iint_{\Omega'} A(r, \theta) r dr d\theta$$

When $r > 7.5$ km it is estimated that $\Omega'_{r>7.5 \text{ km}}$ is covered of 60 % land and 40 % sea.

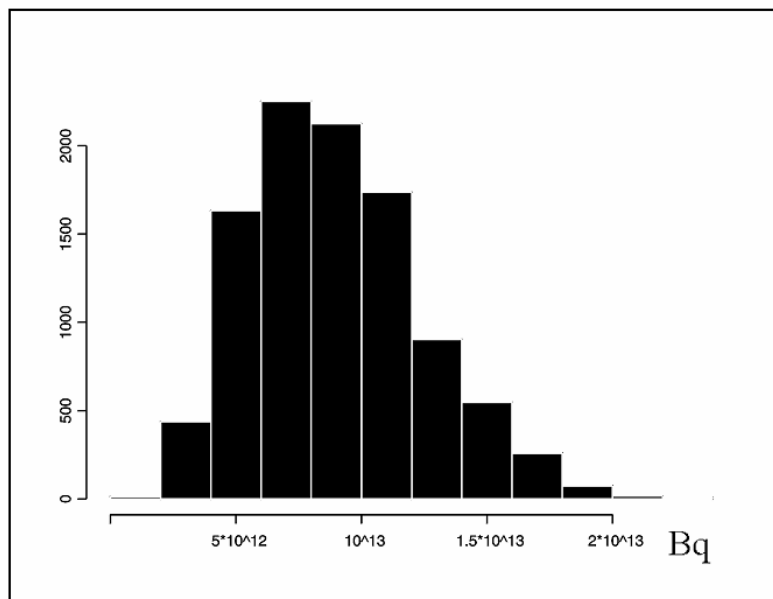
Integration



Total Inventory



Total Inventory



Reported Inventories

- 0.98 TBq (1974)
- 1.21 TBq (1979)
- 1.38 TBq (1984)
- 1.61 TBq (1991)
- 3.9 TBq (1997) HR-alpha-spec.
- 9.5 TBq (1997) This presentation

Discussion

- Calibration ($^{241}\text{Am}/^{239,240}\text{Pu}$ ratio) ?
- Integration area ?
- Fitted function ?

Conclusions

- **Good things**
 - fairly good estimates
 - uncertainties given
 - activity distribution
- **Less good things**
 - detector limit
 - still to few sub-samples

Plutonium Inventory Calculations in Sediments when Hot Particles are present

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Abstract

The inventory of plutonium in marine sediments, originating from the aircraft accident in 1968, in Thule (Greenland) has been calculated. Two different methods have been used for estimating the plutonium inventory in these activity heterogeneous sediments containing hot particles. One of the methods assumes homogenous activity distribution and the activity is determined based on radiochemical separation followed by alpha spectrometry (conventional method). The other method is based on a non destructive technique, measuring the gamma emitting ^{241}Pu daughter ^{241}Am for the determination of $^{239,240}\text{Pu}$. The design of the method makes it possible to evaluate how hot particles effect the inventory.

Plutonium from the accident has been dispersed to a distance of 99.3 km from the point of impact with a dispersion rate of 3.4 km y^{-1} . The Pu activity concentration in the sediment is best described by a bi-exponentially decreasing function of the distance from the point of impact.

The differences between the two total $^{239,240}\text{Pu}$ inventory estimation methods are significant, 9.6 TBq compared to 3.9 TBq. The lower estimate can be partly explained by the method assuming homogenous activity distribution, not using a representative sub-sample and also using an inadequate dissolution method not totally dissolving PuO_2 -complexes.

1 Introduction

It is difficult to calculate an accurate inventory of plutonium in sediments when hot particles are present, as samples are heterogeneous and cannot be homogenised in terms of their activity concentrations. The main problems are outlined below.

1.1 Sampling treatment used previously for Thule sediments

There are several problems when determining activity concentrations of radionuclides in samples containing Pu hot particles. Due to poor resolution in the alpha spectra, the $^{239,240}\text{Pu}$ low energy tail will grow into the yield determinant peak (^{242}Pu) if a hot particle is included in the analyzed sub-sample, which prevented activity determination. In such cases in past studies, replicate samples were

taken until a resolvable spectrum was obtained. Often only one such replicate sample was needed. This procedure inevitably results in an underestimation of the total activity.

Another problem (uncertainty) is that small sub-samples are used because the sediments are highly contaminated. Typically 0.5–1 g of ~ 140 g has been used in determining the activity concentration in the Thule sediment samples. Such a small sub-sample is not representative of the whole sample when the activity is heterogeneously distributed in the slice, which is the case when Pu-hot particles are present.

A third problem is that the particles in the Thule sediments are present as PuO_2 [1]. Plutonium in this chemical form is difficult to dissolve using common chemical dissolution techniques, such as leaching with *Aqua Regia* [2]. Tests have shown that up to 40 % of the Pu activity remains undissolved when the plutonium is in this form [3]. The method used at Risø National Laboratory has been the one described by Talvitie [4], using *Aqua Regia* for leaching plutonium from samples. Therefore we know that the Pu activity in the Thule samples has been underestimated and for that reason the inventory is higher than published. Two of the problems described above (poor alpha resolution and leaching instead of using a total destruction technique) give a maximum measurable activity level of about 0.8 Bq $^{239,240}\text{Pu}$ per sub-sample. The hot particles therefore give rise to an uncertainty when the inventory is calculated.

There is also a fourth problem; sediment mixing caused by bioturbation, which has buried the plutonium deep down in the sediment [5]. The sediment corers used, Gemini and Haps, do not sample to depths below the mixing depth, and so will also result in an underestimate of the inventory. This is mainly a problem in close vicinity to the point of impact, where the plutonium originating from the accident is buried to depths greater than 20 cm. In Figure 2, data from Dahlgaard *et al.* (2001) [6], show depth profiles from the Thule-97 expedition where this effect can be seen.

To avoid the problem of small sub-samples, all of the sediment in each section could be totally dissolved and a small aliquot from the homogeneous activity solution could be used to determine the activity by ordinary alpha-spectrometry or by ICP-MS. However, this can be difficult as the dissolution problem of the PuO_2 -complexes still remains and there are no radiochemical procedures reported of how to totally dissolve 140 g of sediment. It is important to keep in mind that the chemical yield determinant is in another chemical form, often Pu-nitrate. The chemical yield can therefore be very good even though some fractions from the PuO_2 particles may remain undissolved, for that reason the chemical yield calculated can be misleading.

There are relatively few hot particles in the Thule sediments, however, they carry most of the activity, as will be shown later. A method to get a more accurate estimate of the Pu-inventory could be to focus on measuring these. This could be done by gamma-measurement on the gamma emitting ^{241}Pu daughter ^{241}Am in the whole sediment slice sample. By this method the dissolution problem of the PuO_2 -particle is excluded, and fairly large sub-samples could be used to determine the activity, which gives a more representative sub-sample. However, applying this technique to determine the plutonium activity requires that the activity ratios ($^{241}\text{Am}/\text{Pu}$ and $^{241}\text{Pu}/\text{Pu}$) are known in the whole sampling area. In addition, precautions must be taken as the ^{241}Am gamma energy is fairly low ($E_\gamma = 59.6$ keV) and self attenuation in the sample can

be a problem. There are methods describing activity determinations when γ -emitting hot particles are present, i.e. Bunzl [7] and Kashparov *et al.* [8]. They stress the importance of measure the samples several times, mixing the sample between the different measurements, when hot-particles are present and a planar measurement geometry is used. As, if a hot-particle has a geometrically close position to the detector in the measurement geometry, it would overestimate the activity in the sample, and if the particle has a position "far away" one would underestimate the activity. Bunzl [7] also defines that a sample contains a hot particle if the different measurements of the same sample exceed a certain deviation. The magnitude of the deviation depends on the number of mixings performed and on the precision of the activity measurement. A similar study is also presented by Kashparov *et al.* [8]. Nageldinger *et al.* [9] define a hot particle as a material particle of any chemical and radionuclide composition with a size of up to 100 μm and an activity of not less than 4 Bq per particle. Nageldinger *et al.*'s [9] definition is less appropriate for Pu-alpha emitting hot particles as, in any environmental sample 4 Bq Pu would be considered a very high activity. Usually activity levels are 3–6 orders of magnitude lower (mBq– μBq) per sample. The most convenient definition of Pu hot particles in sediment is the one described by Bunzl [7].

1.2 Brief overview of the Thule accident

In January 1968 an aircraft accident involving four nuclear weapons took place in N.W. Greenland. A B-52 bomber, HOB0 28, caught fire and crashed on the sea ice in Bylot Sound, 11 km west of Thule Air Base. Both the aircraft and the four unarmed weapons disintegrated on impact and caused contamination of the surroundings. The non-nuclear explosions were due to the conventional explosive material in the detonators of the weapons. The fissile materials in the weapons were pulverized in the explosion, forming PuO_2 particles. Most of the plutonium was recovered during the clean up program "Crested Ice". However, approximately 3 kg of plutonium was not recovered according to USAF Nuclear Safety report [1] and Strand *et al.* [11]. More detailed descriptions of the accident are published elsewhere, [3, 6, 10].

On the Thule-97 expedition, which is the latest of a series of expeditions, a comprehensive sampling program was performed involving taking 56 double sediment cores, 30 water samples and 134 biota samples. Some of the results are reported elsewhere [6, 13, 14, 15].

Earlier studies in the Thule marine environment have assumed that the few hot particles observed in the sediment do not contribute significantly to the total inventory in the Bylot sound. In this paper, the influence of the hot particles on the plutonium inventory has been studied, based on samples from the Thule-97 expedition, using two different methods. One method assumes a homogenous activity distribution and uses high resolution alpha spectrometry and the other is based on a non destructive screening technique.

2 Material and Methods

2.1 Area studied

The Bylot Sound is located outside the Thule air base, $76^{\circ}33\text{N}$ and $68^{\circ}40\text{W}$ (NW Greenland). The sound is ice covered for about 10 months of the year. The maximum water depth is about 250 meters. The current in the Bylot Sound is predominately tidal [1] and there are two depressions, where fine grained sediments accumulate. The studied area and the sampling stations are indicated in Figure 1. The point of impact is denoted by V2 in the figure.

2.2 Field sampling

A 5 week international sampling cruise to the Thule area took place in August and September 1997. The sediments were mostly sampled by a Gemini corer from the research vessel Adolf-Jensen, but at locations with stony sediment the HAPS sediment corer was used. The sediment cores sampled by the Gemini were sliced into 1 cm slices and the cores sampled by the HAPS into 3 cm thick sections. The slices were frozen and stored in a cold room (-18°C) on the ship in plastic boxes. At some locations it was hard to sample the sea floor because of stones, most likely dropped from passing icebergs and/or because the fine sediment had been washed away by tidal bottom water currents.

2.3 Laboratory treatment

2.3.1 Preparation for alpha spectrometry

In the laboratory, the samples were weighed before freeze drying. The dry weight to wet weight ratios were determined. A one gram sub-sample was taken from every slice for Pu and Am determination. Plutonium and americium were separated using a method described by Talvitie and Holm [4, 16]. The sub-samples were ashed at 700°C for 2 hours, followed by wet ashing with *Aqua Regia*, ion-exchange was then used (AG 1×4 , 100–200 mesh, BIO RAD). ^{242}Pu and ^{243}Am were used as yield determinants. The samples were electrodeposited onto stainless steel discs and measured by passivated implanted planar silicon (PIPS)-detectors. Discs with an activity higher than ~ 0.8 Bq were measured by a special high resolution setup (FWHM < 20 keV) in order to resolve the spike-peak (^{242}Pu) from the $^{239,240}\text{Pu}$ -peak.

Twenty of the samples were wet ashed in a microwave-oven with HF and HNO_3 in order to ensure that the Pu-oxide particles were totally dissolved. These samples were used for absolute calibration of the gamma measurements used in the screening experiment, which is described below.

2.3.2 Preparation for gamma spectroscopy

For the gamma screening experiment, sediment cores from 6 sites were selected. The sites were chosen on the basis that the activity concentration in Bylot Sound decreases exponentially with distance from the point of impact, [17, 18, 19]. The depth of the sediment cores varied between 7 and 20 cm, and they were split into one centimeter slices on board the research vessel Adolf-Jensen. From every sediment slice five aliquots were taken. In order to compare the results

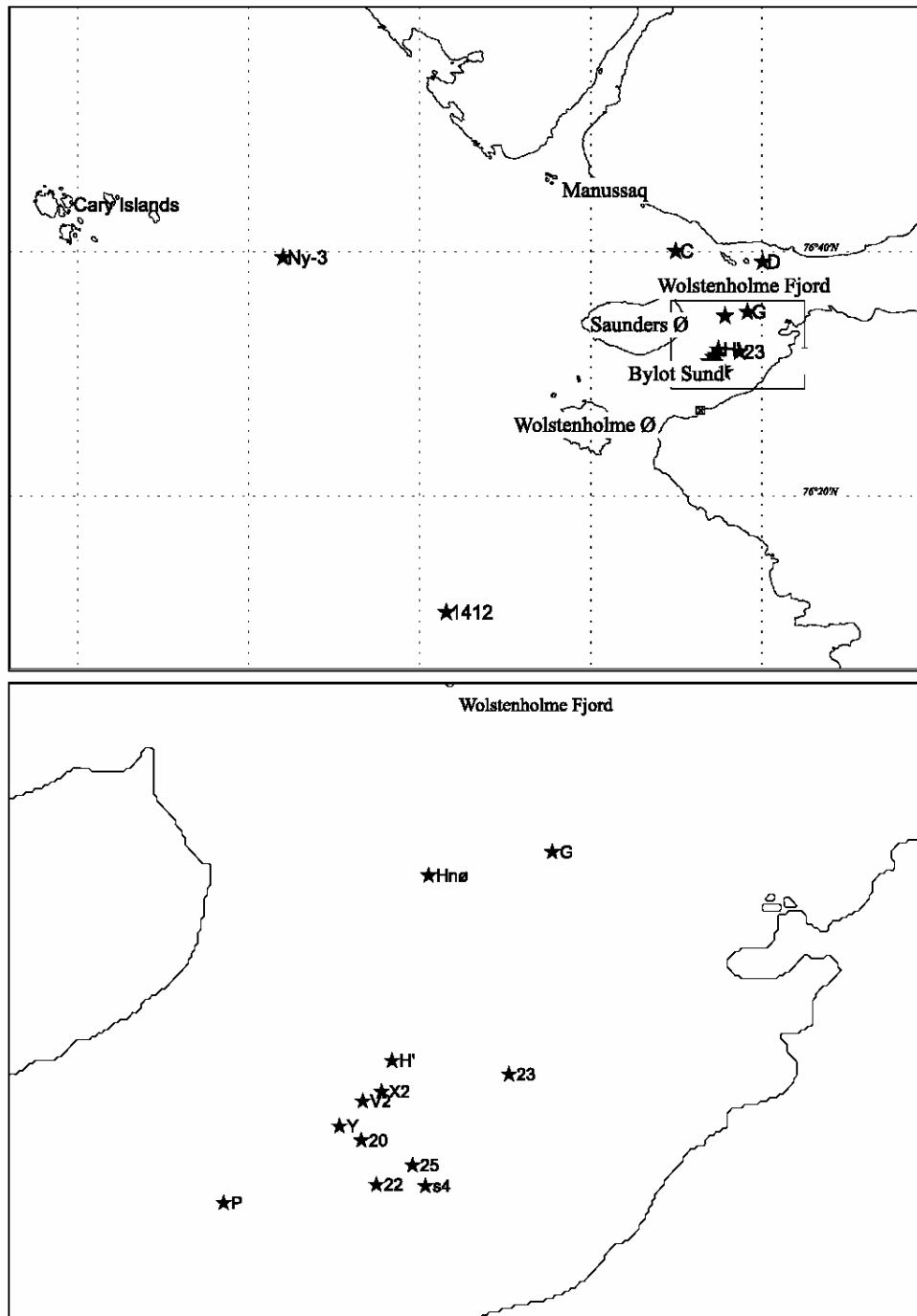


Figure 1: Sampling locations visited at the Thule-97 used in the present paper. Further information of the locations in Table 2. Point of impact is denoted V2.

with earlier expeditions, where the plutonium activity concentrations were based upon 1 g aliquots, and to be able to get an estimate of the variance of the activity concentration, 1 g sub-samples were taken. In total 440 samples were measured. The measurements were performed on a High Purity Germanium (HPGe) well-type detector and the acquisition time was about 3600 seconds. This gives a detection limit of ~ 0.01 Bq ^{241}Am or 0.05 Bq $^{239,240}\text{Pu}$, assuming $^{241}\text{Am}/^{239,240}\text{Pu} = 0.17$. Advantages of using a small cylindrical geometry ($\varnothing = 9$ mm) are that self attenuation is small and that the count-rate is only slightly dependent on the position of the particle in the measured geometry.

The concentrations of ^{137}Cs and ^{210}Pb were determined on large sub-samples (10–15 g). Determination of ^{210}Pb was only performed for cores sampled by the Gemini corer. The measurements were done on HPGe-detectors with efficiencies between 25–40% and a low backgrounds.

2.4 Particle size distribution

The particle size distributions was investigated by autoradiography soon after the accident and the results are presented in the report "Crested Ice" [1]. In the snow sample the geometric mean diameter was $5.6 \mu\text{m}$ and for the ice sample the geometric mean diameter was $2 \mu\text{m}$. The distributions were log-normal¹. As the activity of a particle is proportional to the volume of the particle we have calculated the activity distribution of these particles, by the relationship described in Equation 1.

$$A_{\text{particle}} = \left(\frac{d}{2}\right)^3 \times k \quad (1)$$

where d is the diameter and k is a constant of proportionality.

2.5 Calculations of activity concentrations in the sediment

2.5.1 Conventional determination of Pu activity concentrations in the Thule sediments

For every sediment slice in a core the activity concentration was determined using a 1 g sub-sample from the well-mixed dry powder of the slices, i.e. :

$$A_{\text{slice}} = \frac{A_{\text{sub-sample}}}{m_{\text{sub-sample}}} \quad [\text{Bq kg}^{-1}] \quad (2)$$

where A_{slice} is the activity concentration, $A_{\text{sub-sample}}$ is the activity of the sub-sample and $m_{\text{sub-sample}}$ is the mass of the sub-sample. This activity concentration is then converted to activity per unit area. All the slices are then summed to obtain the inventory at the location:

$$A_{\text{Inventory, core}} = \sum_{i=1}^N A_{\text{activity in slice } i} \quad [\text{Bq m}^{-2}] \quad (3)$$

Here, $A_{\text{activity in slice } i}$ is the activity per unit area of slice i, and N is the number of slices in the core.

¹The notation "log" is in this paper refers to the natural logarithm

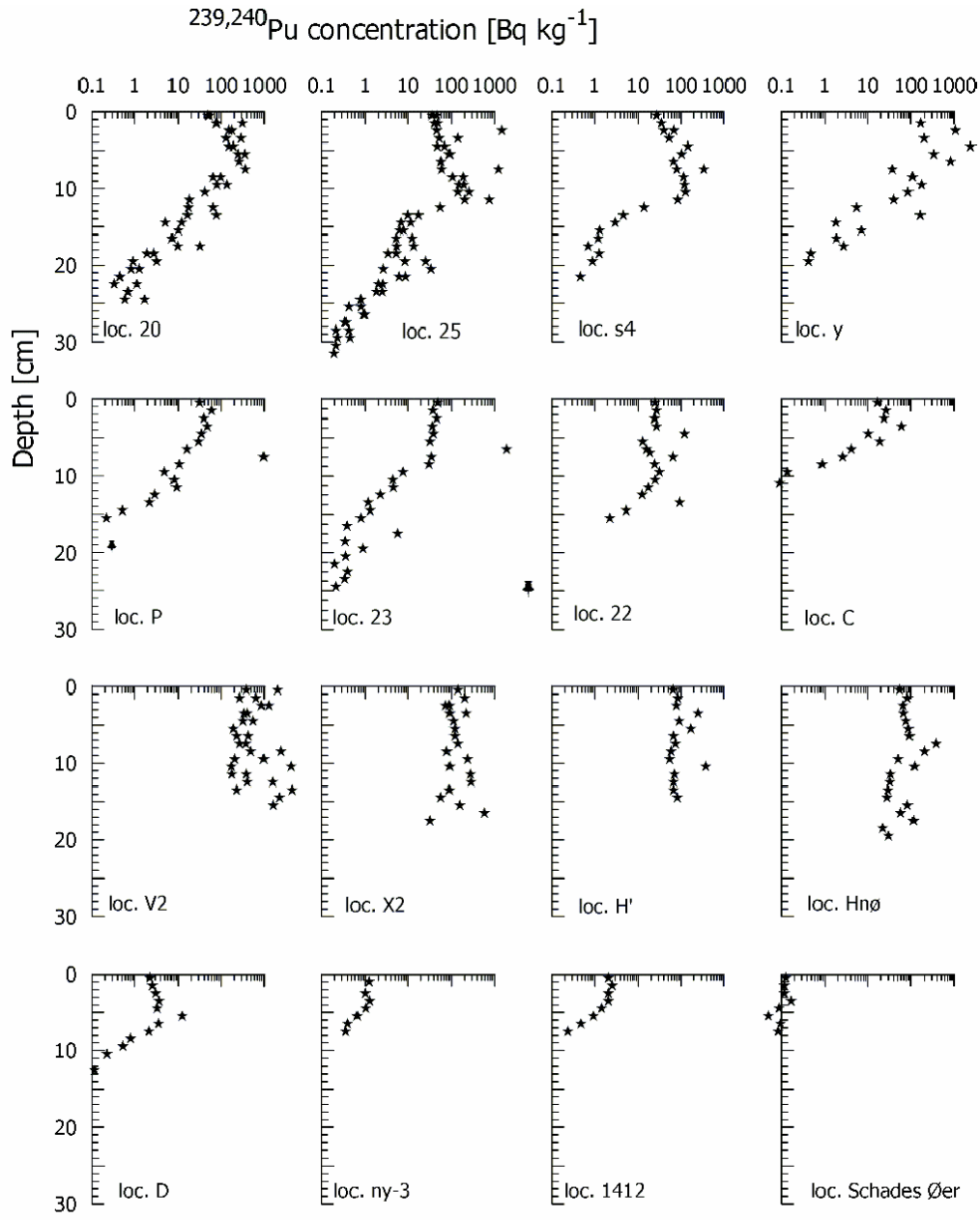


Figure 2: $^{239,240}\text{Pu}$ sediment profiles in sediment cores collected on the Thule-97 expedition. Figure from Dahlgaard et al. [6]

This is the conventional technique for calculating inventories. The technique is trouble-free when the activity distribution is homogeneous in the samples, which is not the case in the Bylot Sound. As an example of the biased evaluation using this technique; In Figure 2 a depth profile from location P (loc. P) can be seen. The calculated inventory at this location is $10\,321\text{ Bq m}^{-2}$, when assuming a homogeneous activity distribution. In this profile, a Pu-peak can be observed at a depth of 7.5 cm. This peak is due to a hot particle in the sub-sample of the sampled slice. When the activity concentration is calculated as in Equation 2, it is assumed that every equal amount of sub-sample contains a particle of this activity. Therefore, using this equation for the slice 7–8 cm at location P results in this slice containing 163 particles (dry weight of the slice = 163.6 grams, $m_{\text{sub-sample}} = 1.000\text{ g}$, $A_{\text{sub-sample}} = 1\text{ Bq}$) and that the other slices contain no particles.

It is obvious that this method does not give a proper picture of the situation and for that reason the inventory calculations are hard to evaluate. The result could also be understood as the total core having 163 particles, and this assumption is only based on one single particle. Particles are found in the sediments across most of the Bylot Sound and for that reason another calculation method of the inventory must be used in order to give a more accurate estimate of the total inventory of the plutonium from the accident. The conventional method only gives an uncertainty estimate from the measurement statistics for the alpha activity determination, and this uncertainty will not give the uncertainty of the number of particles. Also, as has been discussed before, there has been a cutoff in the measurable alpha activity of about 0.8 Bq and the chemical dissolution of Pu from the samples has not been complete, as a fraction will not dissolve.

2.5.2 New method for calculating activity concentrations in sediments when hot particles are present

In this study a screening experiment has been performed with gamma measurements, determining the gamma-emitting ^{241}Am in sub-samples as an indicator of Pu in the sediments, as described in section 2.3.2. The activity concentration, after conversion of Am to Pu, was calculated according to Equation 2 and 3. If the sediment core is sliced in N number of slices and 5 sub-samples from every slice are selected and measured, there are 5^N permutations (different sets of data) of core sets which the inventory can be calculated from, see Figure 3. The design of this survey allows an evaluation of the effect of hot particles on the inventory.

The selection of the core combinations was performed by a monte carlo program written in the statistic-program R [12]. From each site 10 000 core combinations were selected. Each combination includes one of the five gamma measured sub-samples from every sediment slice. This program was also used for calculating the local inventory of each of the six sites and the total inventory in the Bylot Sound.

The advantages of using this method for estimating the inventory are firstly that very high activity samples can be measured, without any cutoff limit in activity concentration as for the alpha measurements. More samples can be measured with a lower cost and a better estimate can be derived with uncertainties of this estimate.

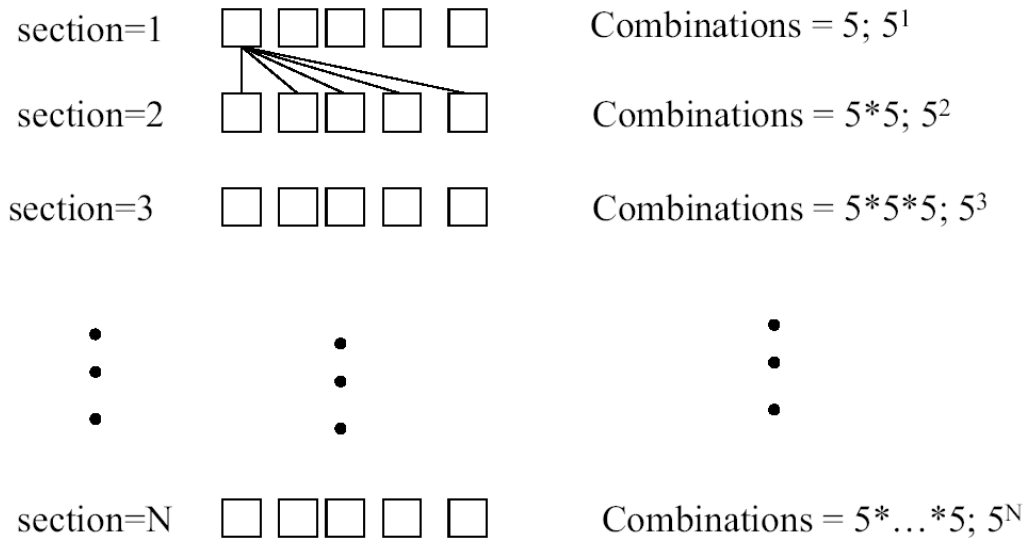


Figure 3: Illustration of the number of core combinations (permutations) that can be derived from a sediment core with N sections which have five measured sub-samples in every section.

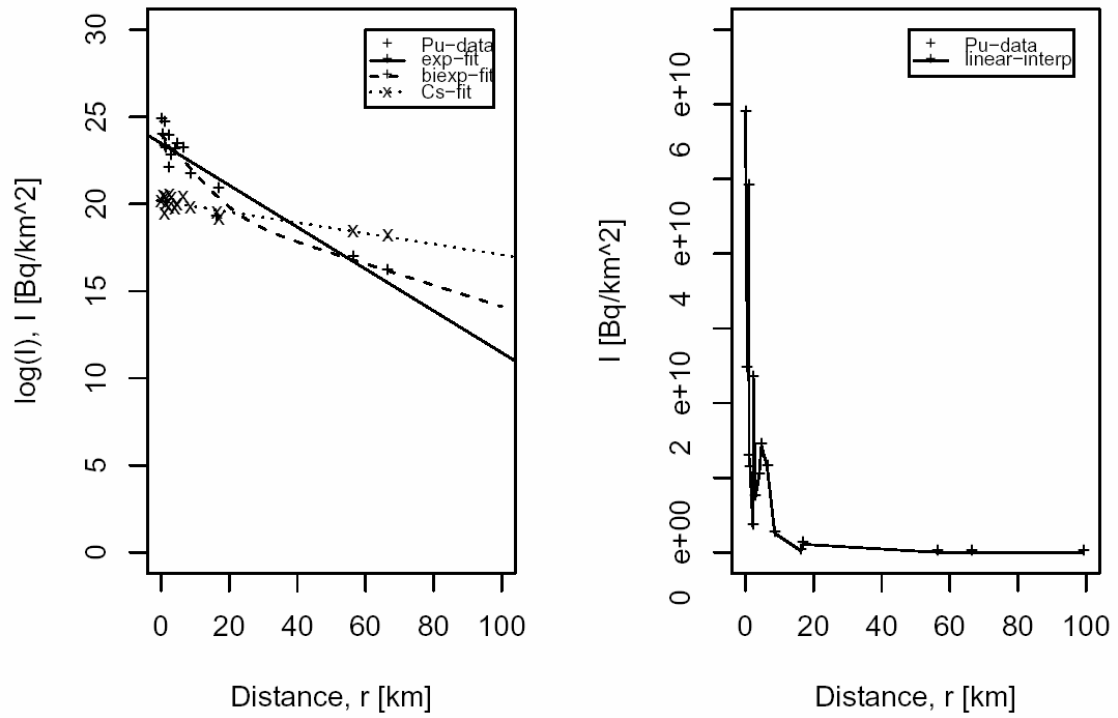


Figure 4: Illustration of the three different fits that have been applied to the local inventories, I [Bq/km^2], versus the distance, r [km]. $^{239,240}\text{Pu}$ data are symbolized with + and the ^{137}Cs data with \times . In the left diagram, which shows the natural logarithm of I , the bi-exponential and exponential fits are shown. To the right the discreet linear interpolated fit is shown.

2.5.3 Calculation of the total Inventory

Total inventory has been calculated using both methods described above. The total accidental plutonium inventory in the sediment has been calculated by integrating a fitted function, $A(r, \theta)$, to the local inventory, see Equation 4. It is assumed that we have equal dispersion of plutonium in all directions. The function, $A(r, \theta)$, is therefore independent of the direction, θ , and depends only on the distance, or radius r , from the point of impact. This assumption has also been applied to earlier estimates of the total inventory, [17, 18]. When the radius, r , is greater than 7.5 km it is estimated that the integrating area, $\Omega_{r>7.5km}^*$, is covered by 60 % land, resulting in 40 % of seafloor to integrate over.

$$\text{Inventory} = \iint_{\Omega} A(x, y) dx dy = \iint_{\Omega^*} A(r, \theta) r dr d\theta \quad (4)$$

The upper integration limit, r_{limit} , is determined by the ratio $^{239,240}\text{Pu}/^{137}\text{Cs}$ equaling the global fallout ratio. In these high arctic sea sediments, a fallout ratio of 0.18 has been applied. This is the decay corrected value, to 1997, as Aarkrog et al. [18] have applied in earlier estimates. The integration limit, or dispersion distance, r_{limit} , was derived from the exponentially fitted functions for $^{239,240}\text{Pu}$ to ^{137}Cs . This means that Equation 4 can be written as:

$$\text{Inventory} = 2\pi \int_{r=0}^{7.5km} A(r) r dr + 0.4 \cdot 2\pi \int_{r>7.5km}^{r_{limit}} A(r) r dr \quad (5)$$

3 Results and Discussion

3.1 Particle size distribution

In Figure 5 the particle activity distributions can be seen in the peak to the left. This is the distribution that occurs if a log-normal distribution of the particle diameter with a mean of $2 \mu\text{m}$ and with a log standard deviation of one is applied. The constant, k , is set to $0.001 \text{ Bq } \mu\text{m}^{-3}$. The calculation of k is derived from studies on single hot particles which will be published elsewhere. From the distributions it can be derived that only 1.3 % of the particles have an activity over the cutoff activity level of 0.8 Bq (equal to a diameter of about $18.5 \mu\text{m}$), however these particles carry about 79 % of the total activity.

These distributions were only valid for the particles found in the contaminated ice area after the accident in 1968. Therefore, they can not simply be applied to all the sediment in this area. It is not clear from the cited references if these particle size distributions were measured before or after the clean up program. If the distributions were valid after the clean up program, it still can not simply be applied to the sediments, as the particle transport through the ice may depend on the size and activity. Also, the sedimentation rate through the water column depends on the size and density of the particles. It is expected

Log-transformed particle size and activity distributions

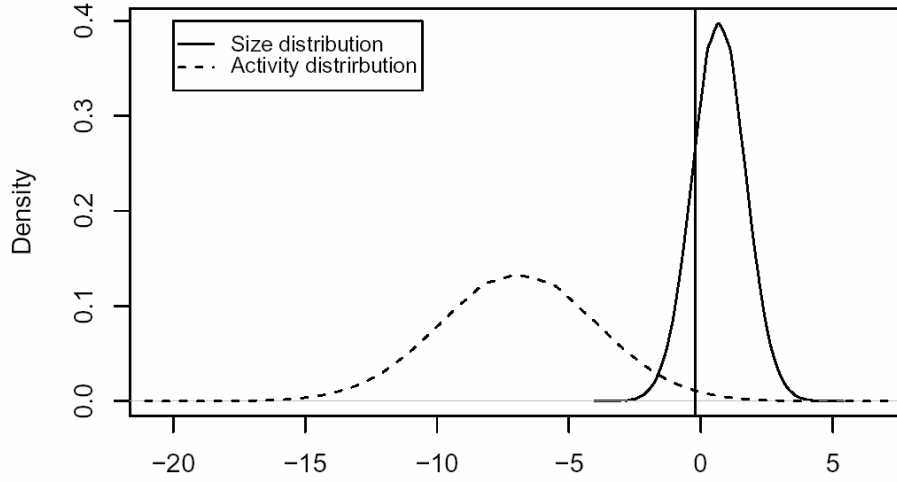


Figure 5: Particle distribution. The solid line shows the log-normal distribution function of the particle diameter (deduced from Project Crested Ice [1]), in μm , of the particles, mean diameter of $2 \mu\text{m}$ and with an log standard deviation of one. The dashed line is the particle activity distribution derived from the size distribution by Equation 1. The mean activity is 0.001 Bq with a log standard deviation of 3. The two distributions are log-transformed.

though, that the largest particles would have settled fastest and thereby also settled closest to the point of impact. Smaller size fractions may have been transported further away by the tidal current and settle to the sediment at greater distances. Therefore, it may be expected that the particle size distribution would be a function of distance from the point of impact and probably the size distribution may have a higher mean value at the point of impact compared with the distribution on the ice. These considerations are important because the few large hot particles carry most of the activity, and for that reason they are very important when inventory estimations are carried out. It is clear, from the results from the Thule-97 expedition as well as earlier expeditions, that the hot particles are mostly found within a 6 km radius from the point of impact.

3.2 Results from the conventional method of calculating the total plutonium inventory in the Bylot Sound, based on alpha spectroscopy.

Table 2 gives inventories of $^{239,240}\text{Pu}$, based on alpha spectroscopy measurements, and of ^{137}Cs determined by γ -spectroscopy. The excess $^{239,240}\text{Pu}$ is derived by subtraction of the expected global fallout plutonium calculated from the ^{137}Cs data and the global fallout ratio. The global fallout ratio $^{239,240}\text{Pu}/^{137}\text{Cs}$ was set to 0.18. It is assumed that Pu has a similar transport mechanism to Cs in the sedimentation process, i.e. near shore sediments have the same global fallout ratio as sediments far from the shore. The ^{137}Cs concentration seems, as has also been observed in earlier investigations [18, 19], to decrease exponentially

as a function of distance from the point of impact. This can be explained by the fact that the crash occurred over one of the depressions in the Bylot Sound where the sedimentation rate may be higher. The fitted exponential function to the ^{137}Cs data in Table 2 is:

$$A(r, \theta) = 567.16 \cdot 10^6 \cdot e^{-0.0308 \cdot r}.$$

The excess Pu data is best fitted to a decreasing bi-exponential function of the distance from the point of impact, instead of a mono-exponential function as have been used in earlier studies. This can be seen in the left diagram in Figure 4, where the excess $^{239,240}\text{Pu}$ is plotted against the distance in a log-diagram. In a study of bioturbation, mixing and resuspension using a bioturbation model, which will be published elsewhere, it is shown that the sampling stations D, 1412 and Ny-3 have mainly been contaminated by recent input of plutonium which originated from the accident. For the other stations it seems as the main contamination occurred soon (until the ice broke up) after the accident. It was observed that when the ice broke up in the summer following the accident, the ice drifted to the north and out of Bylot Sound [1, 10].

These observations may explain the bi-exponential decrease in concentration as a function of distance from the point of impact. The fast decreasing component in the function would then reflect the ice drift where the contaminated ice melted, resulting in the release of particles which sank to the seafloor during the ice drift. The slow component could represent the resuspension from the initially contaminated areas. There is also another compartment, which can be considered to be included in the fast component. This was the very first moment at impact (4:39 p.m. Atlantic Standard Time, 21 January 1968) where an area of about 2500 m² was broken up by the momentum of the impact of the aircraft on the ice and the exploding weapons. Through this hole, which was refrozen quickly, debris from the aircraft and an unknown amount of plutonium were transported to the seawater and the seafloor. The plutonium particles could at this moment have been transported some kilometers away from the impact site as there is a tidal current with a maximum speed of 0.40 knots to the south-south-west and at spring tide, 0.10 knots to the north-north-east.

One explanation that no such bi-exponential function has been observed in earlier studies could be that there has been limited sediment investigations of sites outside the Bylot Sound and that the $^{239,240}\text{Pu}$ and ^{137}Cs data from sampling stations outside the Bylot Sound could not be compared as the nuclides were measured in different sections of the core. As an example, on the Thule-91 expedition measurements were performed to a distance of 8.7 km from the point of impact [19], resulting in one fast decreasing mono-exponential function. There were measurements further away, but the $^{239,240}\text{Pu}/^{137}\text{Cs}$ ratios could not be determined as measurements were performed on different sections of the core.

The first investigations performed in 1968 on accidental plutonium in the Bylot Sound sediments, used a somewhat different method for estimating the total Pu inventory. In that study it was assumed that most of the activity was dispersed within a 30 km² elliptical area centered around the point of impact [10]. From the mean $^{239,240}\text{Pu}$ concentration in this area the total inventory was calculated. The result from this calculation was 3 Ci (0.15 TBq). In addition, the $^{239,240}\text{Pu}$ concentration was based on the uppermost centimeter (0-2 cm) of the sediment. In the second reported investigation [17], the activity concentration was assumed to follow either a mono-exponential function or a power function of distance, i.e. $A(r, \theta) = A_0 \cdot r^{-k}$. These functions were integrated

out to a radius of 45 km. The calculated inventory from these two integrated functions were 29 and 32 Ci (1.4 and 1.5 TBq) respectively.

Eriksson et al. (1999) [15] reported an inventory of 1.7 TBq. This estimate was based on some of the Thule-97 data. However, there were fewer sampling stations included and the electroplated Pu disks with an activity higher than 0.8 Bq had not yet been analyzed in the high resolution alpha spectrometric device. Also, the upper integration limit, r_{limit} , was less than the limit used in the present study as the global fallout ratio used was higher. The inventory calculation was based on an exponential function ($A(r, \theta) = 20.813 \cdot 10^9 \cdot e^{-0.2296 \cdot r}$), which will be shown later in this article to give an under estimation of the total inventory.

As mentioned before, in the present investigation three different functions have been fitted to the $^{239,240}\text{Pu}$ concentration data. Firstly a bi-exponential function, which is assumed to be the most correct, where the $^{239,240}\text{Pu}$ concentration at different distances is given by:

$$A(r, \theta) = 25.945 \cdot 10^9 \cdot e^{-0.2303 \cdot r} + 0.616 \cdot 10^9 \cdot e^{-0.0489 \cdot r}$$

Secondly a single exponential function, to be able to compare the total inventory with earlier estimates, where the $^{239,240}\text{Pu}$ concentration is given by:

$$A(r, \theta) = 14.035 \cdot 10^9 \cdot e^{-0.109 \cdot r}$$

In addition, one discrete function that assumes that the concentration varies linearly between two neighbouring (referring to the distance from the point of impact) sampling stations as:

$$A(r, \theta) = \sum_{i=1}^{15} A_i + k_i r_i$$

The values of A_i , k_i and r_i can be seen in Table 1. The reason for including such a function is that the local inventories at the sampling stations close to the point of impact, $r < 5$ km, do not follow an exponential nor a perfect biexponential curve. This is because of the heterogeneous activity concentrations the data shows. Therefore, in this inner area, the activity concentration can be explained just as well by a linear variation between sampling stations.

The upper integration limit, r_{limit} , was determined from the slowly decreasing component ($\dots 0.616 \cdot 10^9 \cdot e^{-0.0489 \cdot r}$) from the bi-exponential function describing the $^{239,240}\text{Pu}$ concentration and the function describing the ^{137}Cs concentration. Using the global fallout ratio of 0.18 results in that r_{limit} equals to 99.3 km, i.e. the dispersion rate may be estimated to 3.4 km y^{-1} ($99.3 \text{ km}/29 \text{ y}$).

The inventory derived by the alpha measurements can be seen in Table 2 and the inventory integrated to different distances from the point of impact can be seen in Table 5. The three different integrated functions turn out to about 3.9 TBq. This is considerably higher than the inventory reported earlier. This is because the sampling stations Loc 1412 and Ny-3 are included in the calculations, as they have excess plutonium originating from the accident, resulting in that the fitted functions decrease much more slowly. Another explanation of this higher estimate is that a high resolution alpha spectrometry was used, so that re-sampling was not needed. It can be seen in the table that the older estimates of about 1.5 TBq are obtained somewhere between 6.4–7.5 km from the point of impact. The 3.9 TBq estimate could be considered an underestimate for three reasons. Firstly, the radiochemical technique used is insufficient to completely dissolve the Pu-oxide matrices, resulting in that hot particles to a great extent

Table 1: The coefficients A_i and k_i valid in different intervals r_i

i	1	2	3	4	5	6	7	8
$r_i[km]$	0-0.58	0.58-0.94	0.94-1.07	1.07-1.36	1.36-2.21	2.21-2.33	2.33-2.89	2.89-4.01
$A_i[Bq]$	5.88E+07	2.46E+07	4.90E+07	1.28E+07	1.13E+07	3.52E+06	2.33E+07	7.35E+06
$k_i[Bq/km]$	-5.91E+07	6.79E+07	-2.78E+08	-5.20E+06	-9.19E+06	1.65E+08	-2.85E+07	2.59E+06
i	9	10	11	12	13	14	15	16
$r_i[km]$	4.01-4.71	4.71-6.40	6.4-8.6	8.6-16.3	16.3-17	17-56.4	56.4-66.6	66.6-99.3
$A_i[Bq]$	1.03E+07	1.43E+07	1.14E+07	2.58E+06	2.23E+05	1.10E+06	2.11E+04	9.78E+03
$k_i[Bq/km]$	5.80E+06	-1.71E+06	-4.02E+06	-3.06E+05	1.25E+06	-2.74E+04	-1.11E+03	-2.99E+02

are excluded. Secondly, as can be seen in Dahlgaard et al. [6] Figure 4 of Pu depth profiles, that the sediment sampled at stations V2, X2, H' and Hnø do not reach zero activity by the deepest sediment section. In fact these profiles show a constant concentration all throughout the sampled sediment core, i.e. the inventory is underestimated. The third reason is that only one aliquot was used and that this single 1 g aliquot cannot be considered as a representative sub-sample in these activity heterogeneous sediments.

3.3 A new calculation of the total plutonium inventory in the Bylot Sound, based on γ -spectrometry.

To be able to compare the γ -screening experiment with earlier estimates and to confirm that hot particles play an important role for the total inventory, two calculations were performed. The first was when all the data obtained were included, and secondly, the sub-samples with an activity concentration over 1.8 Bq/sample (which was the highest activity measurable by the alpha spectrometric measurements) were set to this value, i.e. exclusion of hot particles. By doing this, the inventory result would be in the same order as the data obtained from the alpha spectrometric measurements.

In Figure 6 the results from the 10 000 calculations of the local inventory from each of the selected 6 sites can be seen.

One would expect to see a log-normal type distribution as several sub-samples were measured which would be expected to include most of the particle sizes. However, as can be seen for the inventory distributions for location V2 (the point of impact) and location P (4.01 km from the point of impact), the inventory distribution is very dependent on the hot particle. Location V2 has several hot particles, 9 of the 70 sub-samples measured have an activity over 1 Bq, but the calculated inventory distribution is dominated by two of these hot particles. One particle is of 50 Bq in slice 10–11 cm and the other is of 153 Bq in slice 4–5 cm depth. In Figure 6 where the inventory distribution at location V2 can be seen, the first peak in the histogram is the distribution when neither of these large hot particles is included in the calculation and the second peak is when the 50 Bq particle is included but not the 153 Bq particle. The third is when the 153 Bq particle is included but not the 50 Bq particle, and the fourth peak is the distribution with both particles included. The probability that one of the particles is included is $1/5$, as there are 5 sub-samples in each sediment slice, and the probability of including both is $1/25$. The inventory distribution at location P is somewhat more difficult to explain. There are 4 particles that dominate the inventory distribution. Three of these are located in the sediment slice 5–6 cm (1.61, 1.62 and 2.79 Bq respectively) and there is one hot particle in the slice 10–11 cm of 2.37 Bq. The first peak is for combinations excluding all of these particles. The second peak is when one of the two particles with activities of 1.61 and 1.62 Bq is included. The third peak is when one of the higher activity particles (2.79 and 2.37 Bq) is included. As three of the particles are in the same sediment slice none of these can be combined and summarized in the inventory calculations but all of them can be combined with the hot particle in slice 10–11 cm and the fourth and fifth peak are representing these combinations, i.e. the forth peak is if either of the 1.61 and 1.62 Bq particles are combined with the 2.37 Bq particle and the fifth peak is the combination of the 2.79 and 2.37 Bq particles.

Table 2: Inventory of $^{239,240}\text{Pu}$ determined by alpha spectroscopy.

Location	Total Pu [Bq/m ²]	Excess Pu [Bq/m ²]	Integrated Excess Pu [%]	^{137}Cs [Bq/m ²]	Location Latitude Longitude	Distance from impact [km]	Water depth [m]
V2	58938	58834	-	575	76°31.366'N 69°17.035'W	0	185
X2	24738	24560	0.9	768	76°31.505'N 69°15.841'W	0.58	181
Y	49072	49020	2.6	289	76°30.997'N 69°18.518'W	0.94	216
20	12973	12841	3.2	735	76°30.789'N 69°17.121'W	1.07	233
H'	11419	11332	3.9	482	76°31.962'N 69°15.176'W	1.36	183
22	3591	3518	5.6	406	76°30.137'N 69°16.167'W	2.21	196
25	23445	23294	6.2	839	76°30.424'N 69°13.876'W	2.33	237
s4	7481	7354	9.7	705	76°30.117'N 69°13.068'W	2.89	241
P	10321	10253	15	378	76°29.869'N 69°25.864'W	4.01	211
23	14397	14312	21	470	76°31.761'N 69°07.760'W	4.71	207
Hnø	11548	11414	40	747	76°34.688'N 69°12.855'W	6.40	199
G	2654	2579	48	415	76°35.032'N 69°05.014'W	8.60	195
D	277	223	55	302	76°39.115'N 68°59.652'W	16.3	89
C	1138	1099	56	215	76°39.993'N 69°30.179'W	17	120
1412	40	21.1	98	105	76°10.488'N 70°50.687'W	56.4	640
Ny-3	24	9.78	99	79	76°39.485'N 71°47.955'W	66.6	505

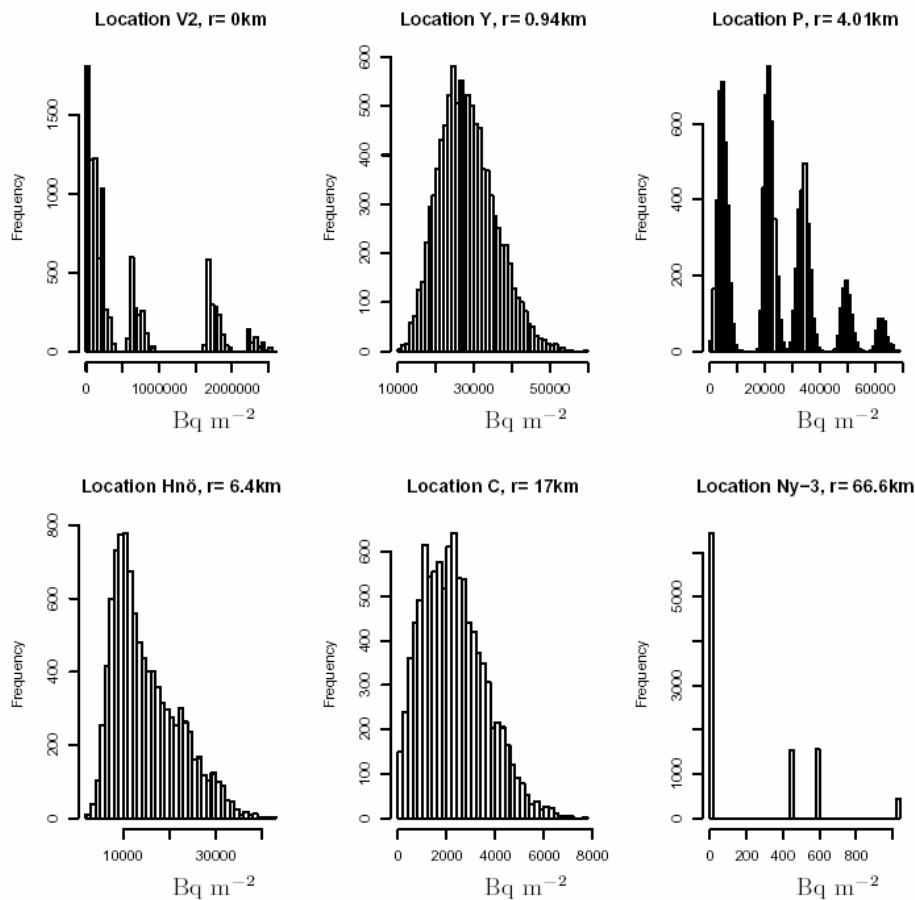


Figure 6: $^{239,240}\text{Pu}$ inventory distributions calculated from 10 000 sediment core combinations (permutations). It is clear that the distributions for locations V2 and P are highly influenced by hot particles. The statistics for each distribution can be seen in Table 3

At location Ny-3 only 2 of the 35 measured sub-samples were over a detectable level, however, these two measurements are considered as outliers. The activity at this location was too low to make any reasonable assessment of the local inventory and no hot particles appear to have been transported to this location. Therefore, the alpha spectrometric determined activity concentrations were used in the calculation procedure of the total inventory, see below.

The statistics for the local inventory distributions in Figure 6 can be seen in Table 3. As the distributions are not normal distributions, the standard deviations from the mean value have limited value. The results are instead represented with the minimum, maximum, mean and the median values. The first quadrant (1st Qu.) and the third quadrant (3rd Qu.) values are also included in the Table².

In Figure 7 the distributions obtained when a cutoff of 1.8 Bq/sample was

²50 % of the results, with the center median value, are included between the 1st and the 3rd quartile.

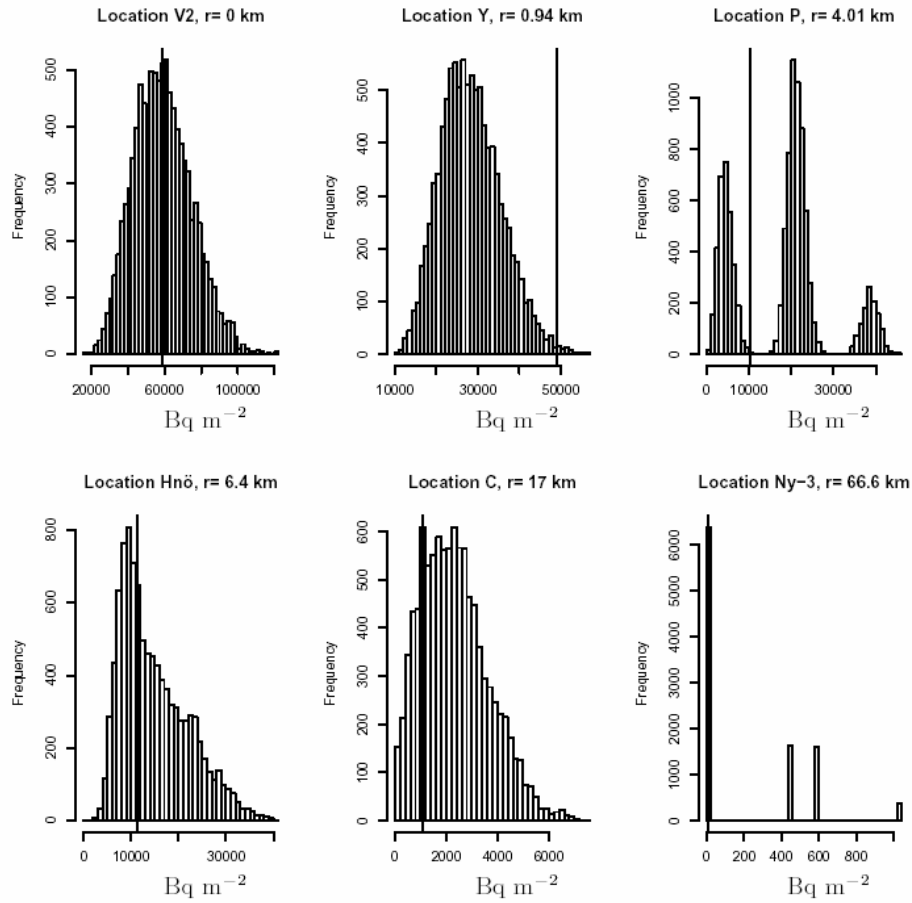


Figure 7: $^{239,240}\text{Pu}$ inventory distributions calculated as in Figure 6, but with a cutoff of 1.8 Bq/sample. The vertical lines indicate the inventory determined by alpha spectrometry. The statistics for each distribution can be seen in Table 4

applied. The vertical line in each distribution is the local inventory obtained from the alpha spectrometric measurements. The gamma screening results, when the cutoff is applied, is in accordance with the alpha spectrometric results, which support the hypotheses that the earlier estimates of local inventory have underestimated the amount of plutonium. It is also clear that the hot particles play an important role at the locations close to the point of impact. For that reason, when determinations of Pu inventory are to be done close to the point of impact, the gamma screening technique should be used instead of the commonly used alpha spectrometric technique, whereas at locations Hnø and C either method of estimating the inventory can be used. At location Ny-3 the gamma screening technique of the sediment core is of no use and alpha spectrometric methods must be used to derive the activity concentrations.

A synthesis of the calculated total accidental inventories of $^{239,240}\text{Pu}$ is given in Figure 8. The different Pu inventory distributions are derived from 10 000 integrations of the 10 000 fitted curves for each of the different fitted functions.

Table 3: $^{239,240}\text{Pu}$ inventories [Bq m^{-2}] statistic summary of the distributions from Figure 6.

	Min	1st Qu.	Median	Mean	3rd Qu.	Max.
Location						
V2	15270	68930	212200	561100	722800	2561000
Y	10090	22920	27640	28250	32980	59940
P	356.1	5942	21820	23040	33860	68870
Hnø	2247	9456	13120	14940	19520	42600
C	0	1277	2167	2290	3110	7630
Ny-3	0	0	0	205.5	446.4	1028

Table 4: $^{239,240}\text{Pu}$ inventories [Bq m^{-2}] statistic summary of the distributions from the Figure 7, when a cutoff of 1.8 Bq is applied. The figures are in Bq m^{-2} .

	Min	1st Qu.	Median	Mean	3rd Qu.	Max.
Location						
V2	17420.0	49860	61010	62170.0	73170.0	125500
Y	11190.0	22960	27240	28010.0	32360.0	53450
P	356.1	5490	20670	17940.0	23130.0	45940
Hnø	2826.0	9466	13000	14780.0	19220.0	39370
C	0.0	1292	2179	2313.0	3152.0	7593
Ny-3	0.0	0	0	202.9	446.4	1028

The histograms A (bi-exponential fit), B (exponential fit) and C (discrete function fit) are the real distributions when the data do not have any cutoff limit and D, E and F are the corresponding inventory distributions obtained when a cutoff of 1.8 Bq/sample is applied. In Tables 6 and 7 the statistics for each distribution can be seen. The tables also represent inventories out to different radiuses from the point of impact. The total estimated inventory statistics can be seen in the column with the header 0–99.6 km in each table. The median values for the total inventory is 9.5 TBq (1st Qu. = 6.7 TBq and 3rd Qu. = 13.2 TBq) for the bi-exponential fitted functions and 8.7 TBq (1st Qu. = 6.9 TBq and 3rd Qu. = 11.2 TBq) for the exponential fitted functions. In Table 6 it can be seen that the exponential fitted integration gives the lower value close to the point of impact and that the bi-exponential and the linear fitted integrations give equal amount of plutonium. The linear fitted integration probably overestimates the amount of plutonium at distances over 17 km as no real physical explanation for such dispersion can be given.

One criticism of these inventory estimations could be that only 6 sites are included. When a cutoff of 1.8 Bq/sample has been applied, the inventory agrees well with the data obtained from the alpha spectrometric measurements. However, the total inventory for the alpha spectrometric measurements is about 1.7 times higher when only the 6 sampling sites used in the gamma screening experiment are considered in the integration ("Exp-fit,6p" in Table 5), compared to if all sites are included ("Exp-fit" in Table 5). For that reason the total inventory calculated from the gamma screening experiment may be overestimated by a factor of 1.7. However, 2 of the 6 sites (V2 and Hnø) have underestimated

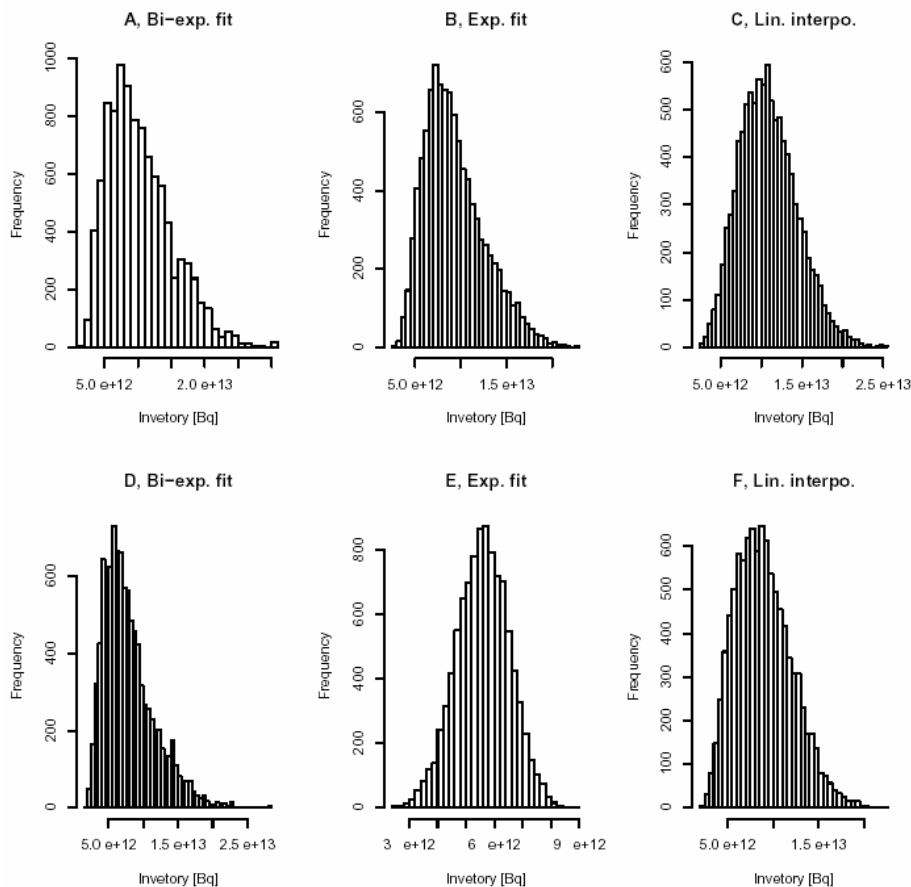


Figure 8: Histogram of the $^{239,240}\text{Pu}$ inventories [Bq] based on 10 000 integrations. Histogram A, B and C are derived with no cutoff of the activity in the sub-sample. For histogram D, E and F a cutoff of 1.8 Bq/sample is used. The statistics for the total inventory results are seen in Tables 6 and 7 in the column with the header, 0–99.3 km.

inventories as the sampled sediment cores have not reached background activity levels, see Figure 2. So the correction factor of 1.7 is overestimated.

4 Conclusions

This study illustrates the difficulties in determining activity concentrations and inventories in areas contaminated with hot particles. The key problem in these areas is deciding what should be considered a representative sample for the inventory calculation. Specific problems for the high arctic environment are the remote location and difficult sampling conditions with severe weather and drifting ice which sometimes make sampling impossible, and that the nuclides studied are mostly alpha emitters. In general, the problem of estimating the inventory in heterogeneously contaminated areas is more difficult for alpha emitting nuclides

Table 5: $^{239,240}\text{Pu}$ inventory [Bq] calculated from alpha measurements at different distances derived by three different fit methods. Exp-fit,6p is the Integrated function $A(r, \theta) = 28.028 \cdot 10^9 \cdot e^{-0.1243 \cdot r}$

From Alpha	0-0.94 km	0-4.01 km	0-6.4 km	0-7.5 km	0-17 km	0-66.6 km	0-99.3 km
Biexp-fit							
Min.	8.966e+10	7.023e+11	1.365e+12	1.697e+12	2.748e+12	3.848e+12	3.856e+12
1st Qu.	4.030e+10	5.772e+11	1.227e+12	1.553e+12	2.583e+12	3.653e+12	3.661e+12
Median	1.029e+11	5.994e+11	1.590e+12	2.030e+12	2.463e+12	4.172e+12	4.203e+12
Linear-fit							
Min.	7.200e+10	1.023e+12	2.161e+12	2.728e+12	4.481e+12	6.185e+12	6.196e+12
1st Qu.							
Median							
Mean							
3rd Qu.							
Max.							

Table 6: $^{239,240}\text{Pu}$ inventory [Bq] statistics at different distances derived by three different fit methods without cut of the activity level.

	0-0.94 km	0-4.01 km	0-6.4 km	0-7.5 km	0-17 km	0-66.6 km	0-99.3 km
Biexp-fit							
Min.	3.677e+10	3.669e+11	6.510e+11	8.024e+11	1.346e+12	1.846e+12	1.847e+12
1st Qu.	1.243e+11	6.775e+11	1.220e+12	1.504e+12	2.716e+12	6.383e+12	6.729e+12
Median	1.837e+11	8.225e+11	1.489e+12	1.834e+12	3.385e+12	8.689e+12	9.553e+12
Mean	2.522e+11	8.965e+11	1.658e+12	2.066e+12	3.727e+12	9.273e+12	1.031e+13
3rd Qu.	3.428e+11	1.029e+12	1.859e+12	2.356e+12	4.511e+12	1.161e+13	1.318e+13
Max.	7.789e+11	2.084e+12	3.996e+12	5.015e+12	9.570e+12	2.612e+13	3.051e+13
Exp-fit							
Min.	2.601e+10	3.774e+11	8.097e+11	1.029e+12	1.745e+12	2.572e+12	2.580e+12
1st Qu.	8.042e+10	1.142e+12	2.412e+12	3.042e+12	4.998e+12	6.904e+12	6.914e+12
Median	1.089e+11	1.529e+12	3.205e+12	4.031e+12	6.505e+12	8.731e+12	8.741e+12
Mean	1.199e+11	1.673e+12	3.492e+12	4.384e+12	7.028e+12	9.312e+12	9.323e+12
3rd Qu.	1.496e+11	2.078e+12	4.318e+12	5.411e+12	8.594e+12	1.122e+13	1.123e+13
Max.	3.441e+11	4.671e+12	9.550e+12	1.188e+13	1.831e+13	2.274e+13	2.275e+13
Linear-fit							
Min.	4.283e+10	4.134e+11	8.034e+11	1.041e+12	1.791e+12	2.514e+12	2.545e+12
1st Qu.	1.198e+11	1.176e+12	2.302e+12	2.911e+12	4.599e+12	8.261e+12	8.292e+12
Median	2.436e+11	1.598e+12	3.137e+12	3.792e+12	5.864e+12	1.056e+13	1.059e+13
Mean	5.715e+11	1.770e+12	3.231e+12	3.916e+12	6.030e+12	1.085e+13	1.088e+13
3rd Qu.	7.251e+11	2.268e+12	4.053e+12	4.821e+12	7.253e+12	1.310e+13	1.313e+13
Max.	2.410e+12	4.788e+12	7.976e+12	9.149e+12	1.348e+13	2.540e+13	2.543e+13

Table 7: $^{239,240}\text{Pu}$ inventory [Bq] at different distances derived by three different fit methods with a cutoff of 1.8 Bq/sample.

	0-0.94 km	0-4.01 km	0-6.4 km	0-7.5 km	0-17 km	0-66.6 km	0-99.3 km
Biexp-fit							
Min.	3.958e+10	3.314e+11	6.288e+11	8.034e+11	1.331e+12	1.650e+12	1.650e+12
1st Qu.	7.363e+10	6.702e+11	1.298e+12	1.622e+12	2.794e+12	5.130e+12	5.253e+12
Median	8.254e+10	7.728e+11	1.524e+12	1.906e+12	3.314e+12	6.762e+12	7.126e+12
Mean	8.281e+10	7.792e+11	1.530e+12	1.914e+12	3.355e+12	7.278e+12	7.924e+12
3rd Qu.	9.158e+10	8.780e+11	1.738e+12	2.177e+12	3.846e+12	8.956e+12	9.710e+12
Max.	1.585e+11	1.511e+12	3.096e+12	3.876e+12	6.208e+12	2.156e+13	2.825e+13
Exp-fit							
Min.	2.287e+10	3.355e+11	7.257e+11	9.256e+11	1.592e+12	2.421e+12	2.432e+12
1st Qu.	5.287e+10	7.616e+11	1.625e+12	2.059e+12	3.448e+12	4.949e+12	4.961e+12
Median	6.080e+10	8.724e+11	1.855e+12	2.350e+12	3.926e+12	5.592e+12	5.605e+12
Mean	6.081e+10	8.725e+11	1.857e+12	2.352e+12	3.921e+12	5.579e+12	5.592e+12
3rd Qu.	6.873e+10	9.839e+11	2.091e+12	2.646e+12	4.402e+12	6.226e+12	6.239e+12
Max.	1.044e+11	1.479e+12	3.119e+12	3.935e+12	6.439e+12	8.828e+12	8.842e+12
Linear-fit							
Min.	4.553e+10	3.528e+11	6.791e+11	9.761e+11	1.725e+12	2.318e+12	2.349e+12
1st Qu.	7.836e+10	7.335e+11	1.467e+12	1.938e+12	3.413e+12	6.566e+12	6.598e+12
Median	8.662e+10	8.493e+11	1.706e+12	2.248e+12	3.980e+12	8.614e+12	8.645e+12
Mean	8.701e+10	8.575e+11	1.719e+12	2.270e+12	4.049e+12	8.913e+12	8.944e+12
3rd Qu.	9.535e+10	9.744e+11	1.953e+12	2.575e+12	4.619e+12	1.091e+13	1.094e+13
Max.	1.347e+11	1.595e+12	3.175e+12	4.120e+12	7.401e+12	2.205e+13	2.208e+13

than for other types of radiation. Another problem is that, in close vicinity to the point of impact, the activity distribution of the hot particles, which play an important role for the inventory, is unknown.

This study shows that earlier estimates have underestimated the total inventory in sediments in the Bylot Sound. The main reason for this is that the exponential curve fitted has been based on too few data points far away from the point of impact, resulting in that the slow component has not been considered. Earlier studies have also underestimated the importance of hot particles and treated the samples as if the activity distribution was homogeneous.

A general conclusion is that it is very important to know the amount and composition of hot particles in the sediment, i.e. number of particles, particle size distribution and chemical composition, in order to perform an adequate inventory estimation. Having a true log-normal activity distribution, by sampling from this distribution the calculated mean, used for such area, is most likely underestimated compared with the true mean, as the probability to sample the very few large hot particles is very low.

This study therefore concludes that the inventory is within the range of 5–15 TBq, probably close to 10 TBq, i.e. about 3.8 kg $^{239,240}\text{Pu}$. This is close to the earlier estimated missed amount of 3 kg [1, 11]. Furthermore, in upcoming investigations in the Bylot Sound sediments, the activity determination should be based on a gamma screening technique out to a distance of 17 km from the point of impact and, at distances over 17 km, alpha spectroscopy should be used.

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Title	Theory of Sampling. A mini seminar under the NKS project SAMPSTRAT
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Abstract	<p>At an emergency situation a large number of matrixes can be contaminated and samples of these different matrixes will be collected. These sample matrixes might be or often certainly are heterogeneous and in general more unevenly distributed than from nuclear test fallout or even the Chernobyl accident. On basis of the reported data conclusions and remedial actions causing social and economical costs for the society are taken. Therefore the number of samples from each site, their size and further homogenisations is of great importance. In the case of an emergency situation the activities are generally high and the errors due to counting statistics are small. We could also imagine a situation when a certain nuclear enterprise/activity has to close down or being prosecuted, based on sampling and analysis, for not following directives of discarding radioactivity in the environment. We therefore organized a seminar focusing on the above mentioned problems.</p> <p>The seminar covered several important topics such as an introduction to Theory of sampling (TOS), Lot heterogeneity and sampling in practice, Statistics for sampling in analytical chemistry, Representative mass reduction in sampling.</p> <p>Case studies were presented such as Sampling of heterogeneous bottom ash from municipal waste-incineration plants and Sampling and inventories at Thule Greenland, which also illustrated the difficulties with Plutonium Inventory Calculations in Sediments when Hot Particles were present.</p>
Key words	Sampling, Sampling characteristics, Small sub sampling, Heterogeneous, Particles, Theory of Sampling, TOS, Municipal waste, Bottom ash, Data analysis reliability, variances, Statistics of counting, The minimum practical error, Measuring limitations